D. Klemm, B. Philipp, T. Heinze, U. Heinze,
W. Wagenknecht

Comprehensive Cellulose Chemistry
Volume 1

Fundamentals and Analytical Methods

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Preface

Cellulose, as the most abundant organic polymer, has served mankind for thousands of years as an indispensable material for clothing and housing, and has formed a large part of human culture since the Egyptian papyri. In contrast with cellulose application as a natural product, the use of this polymer as a chemical raw material started just 150 years ago with the discovery of the first cellulose derivatives, but subsequently developed to a production volume of more than 5 million tons annually during this century. At the same time the classical areas of processing cellulose as a natural product by mechanical technologies, for example the manufacture of textile goods from cotton, received a strong impetus by combining them with chemical processes to improve product quality. This line of progress is closely related to and often originated from the development of a systematic chemistry of cellulose comprising predominantly the chemical transformation of the macromolecule.

The knowledge acquired in this area was compiled during this century in a number of monographs and text books still serving as a valuable scientific background in today's cellulose research. But most of these books were published several decades ago, and thus could not take into account recent developments, for example the relevance of ecological problems in cellulose processing, discussion of the advantages and shortcomings of natural resources in general, or today's boom in synthetic organic and supramolecular chemistry. Besides this, some of these books consider only a special field or reflect a rather special point of view. In the authors' opinion, no text book or monograph on the organic chemistry of cellulose is available now, that presents in a comprehensive and still conveniently readable manner the theoretical background and the experimental state of the art at the end of this century.

It is the intention to fill this gap by the two volumes of this book, centered on the routes and the mechanisms of cellulose functionalization, but covering also the close interrelation between a heterogeneous cellulose reaction and the supramolecular structure of this polymer. Special emphasis has been put on distribution of functional groups in relation to reaction conditions and on analytical techniques for their characterization. Not only recent efforts in cellulose research and development are presented and cited but also important results on the last centuries actual up to now are included in order to give a comprehensive description of the chemistry of cellulose.

The authors are indebted to WILEY–VCH Verlag for agreeing to a two-volume presentation, allowing accuracy and readability of the text to be combined, and also leaving enough space for numerous experimental procedures, that are suitable for making a graduate student familiar with the practical laboratory work in cellulose chemistry. From a didactic point of view, as well as for the sake of convenient information retrieval, the authors found it appropriate to survey in the first volume some aspects of cellulose of a more general nature relevant to chemical reactions. Included are e.g. its properties and structure in relation to reactivity, the processes of swelling and dissolution, with their consequences to chemical reactions, and the pathways of cellulose degradation accompanying chemical transformations of this polymer. Special emphasis is given in this part to aspects of physical chemistry and colloid chemistry. A rather detailed presentation of cellulose analytics for characterizing the original polymer and its derivatives at the various structural levels is also included in Volume I. Volume II deals with the various classes of cellulose derivatives, with emphasis on the reaction mechanisms and distribution of functional groups, including, in addition, in each of the chapters also a brief abridgment of relevant industrial processes and an overview of properties and areas of application of the products in question. In both volumes results obtained by the authors' groups are adequately accentuated, especially with regard to Figures and Tables.

It is hoped that the two volumes of this book will be accepted as a useful textbook by graduate students in science, with special interest in cellulosics, and that it will serve as a comprehensive source of information for chemists, physicists, biologists, and engineers professionally engaged with this polymer. The authors' work would find its best appreciation, if the book helps to stimulate young scientists to professional activities in cellulose chemistry, which offers a challenge to innovative ideas and new experimental pathways, also into the next century.

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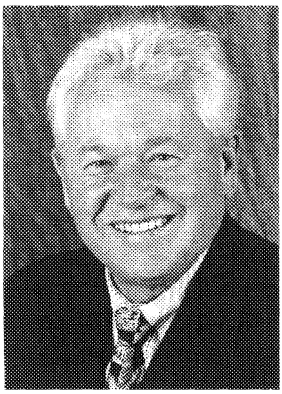
Dieter Klemm



Dieter Klemm, born 1939 in Jena (Germany), studied Chemistry at the University of Jena and received the Masters Degree (diploma) in 1964. With a thesis on stereospecific synthesis of nitrogen-containing steroids he got his Ph.D. degree and has been affiliated with the Institute of Organic Chemistry of the Friedrich-Schiller-University of Jena. In 1977 he obtained the university lecturing qualification (habilitation) with a thesis on photochemistry of *o*-nitrobenzyl compounds in solutions and in polymer matrices and was engaged in the field of synthetic polymer chemistry. In 1980 he moved to the pharmaceutical industry, working there on the synthesis and properties of modified penicillins.

Since 1987 he has been Professor of Organic Chemistry at the university of Jena and active in organic chemistry, carbohydrate research, and bioorganic chemistry. From 1990 to 1993 he was head of the Institute of Organic and Macromolecular Chemistry and since 1996 he co-ordinates a german-wide focus program entitled "Cellulose and cellulose derivatives – molecular and supramolecular structure design" sponsored by the "Deutsche Forschungsgemeinschaft".

The scientific activities of D. Klemm in the last ten years are centered on the organic chemistry of cellulose, especially on new concepts and synthesis pathways in regioselective cellulose functionalization, structure analysis, and preparation of supramolecular structures like ultrathin layers and recognition devices. He is the author of 150 papers, 50 patents, and many invited lectures on organic and polysaccharide chemistry including results on regiocontrol by activation and protection, new approaches to advanced polymers by selective functionalization, synthesis and subsequent reactions of silylcelluloses, arylmethylethers and readily hydrolysable cellulose esters, and the synthesis and properties of bacterial cellulose.

Burkart Philipp

Burkart Philipp, born 1925 in Pirna (Germany), received his diploma in chemistry at the Technical University of Dresden in 1950 and got his Ph.D. from the same university in 1952, with a thesis on the kinetics and mechanism of vapor sorption and swelling of cellulose. Since 1953 he has been affiliated with the Institute of Fibre Research (later Institute of Polymer Chemistry) in Teltow-Seehof, working there as the head of the institute from 1969 to 1981 and again 1990/91. In 1956 he presented his habilitations thesis on the kinetics of the xanthogenate reaction of cellulose at the Technical University of Dresden and lectured there as a part time professor on the chemistry, physics and technology of polymers. During the conversion of the Institute in Teltow-Seehof to a modern polymer research center in 1990 he was a member of the founding commission of the new Max-Planck-Institute of Colloid and Interface Research and an adviser to the Fraunhofer Institute of Applied Polymer Research. In 1994 he received the Hermann Staudinger award in Macromolecular Chemistry from the German Chemical Society (Gesellschaft Deutscher Chemiker). Since his retirement in 1994 he is still affiliated with the Max-Planck-Institute in Teltow-Seehof.

The scientific activities of B. Philipp are centered on the chemistry, physics and technology of cellulose by contributing more than 500 publications, many invited lectures and numerous patents on the chemistry and technology of the viscose process, the chemistry of cellulose dissolution and cellulose degradation, the interaction between cellulose physical structure and reactivity in cellulose derivatization, and, especially in recent years, new routes of selective cellulose functionalization.

Thomas Heinze

Thomas Heinze was born in Plauen (Germany) on July 22, 1958. He studied Chemistry at the Friedrich Schiller University in Jena and received his Maters Degree in Chemistry (diploma) in 1985. After receiving his Ph.D. degree on immobilization of biocides on polymeric carriers under the tutelage of Dieter Klemm in 1989, he worked as a scientific manager for Research and Development in the Faculty of Chemistry at the University of Jena. After 1 year as an EU postdoctoral fellow with Hugo Berghmans at the Catholic University of Leuven (Belgium), he moved back to the University of Jena and obtained a university lecturing qualification with a thesis on new functional ionic polymers from cellulose in 1997.

At present, the scientific activities of Th. Heinze are focused on chemistry and structure analysis of polysaccharides. The work is centered on new synthesis concepts in polyglucan chemistry, on products with unconventional functional groups (photoactive polymers, reactive networks and supramolecular structures, polymer gels), and on polysaccharide polyelectrolytes. He is the author of 60 papers, numerous invited lectures in the field of polysaccharides and Editor of the ACS Series book "Cellulose Derivatives: Synthesis, Cheracterization, and Nanostructures".

Ute Heinze

Ute Heinze was born in Jena (Germany) on December 14, 1961. She studied Chemistry at the Friedrich Schiller University of Jena and received a Masters Degree in Chemistry (diploma) on photophysical investigations of monomeric photoconductors. From 1985 to 1991 she was affiliated with the ceramic industry, dealing with preparation and analysis of special ferrites. In 1991 she moved to the Institute of Organic Chemistry of the Friedrich Schiller University of Jena working there on synthesis and characterization of cellulose derivatives, as well as on microcapsulation of magnetic ferrous oxides/biologically active substances with polysaccharides for developing controlled released pharmaceuticals.

At present she is studying for a Ph.D. in Organic Chemistry, under the supervision of Prof. Dr. D. Klemm. Her thesis has been submitted in 1997. She is the author of eight publications and three patents.

Wolfgang Wagenknecht

Wolfgang Wagenknecht, born 1945 in Güstrow (Germany), received his academic education at the Technical University of Magdeburg and got his diploma in chemistry in 1970. From 1971 to 1991 he was affiliated with the Institute of Polymer Chemistry in Teltow-Seehof, where he presented in 1976 his Ph.D. thesis on swelling and dissolution of cellulose in nonaqueous media. Since 1992 he has worked as a senior scientist in the polysaccharide department of the Fraunhofer-Institute of Applied Polymer Research in Teltow-Seehof.

The scientific activities of Dr. Wagenknecht are centered on the interaction of cellulose with nonaqueous systems, regarding kinetics and mechanism of swelling, as well as dissolution and structure formation from systems of this kind. Results of his work are e.g. new nonaqueous solvent systems for cellulose, the preparation of special types of bead-shaped cellulosics, and the scaling up of new routes of cellulose derivatization including the aplicational testing of the products obtained in the biomedical and environmental area. Dr. Wagenknecht is an expert in selective cellulose functionalization, especially to anionic esters. So far he authored 76 publications, presented numerous invited lectures and holds 45 patents in cellulose dissolution and derivatization.

Acknowledgement

The authors gratefully acknowledge the cooperation of numerous colleagues from academic institutions and from industry, ranging from helpful discussions to supply of relevant data and literature. Especially to be mentioned are Prof. Dr. Albrecht (Akzo Wuppertal), Dr. Balser (Wolff-Walsrode AG), Dr. Carstens (Rhône-Poulance Rhodia AG), Prof. Dr. Fischer (TU Dresden/Hoechst AG), Prof. Dr. Klüfers (University of Karlsruhe), Prof. Dr. Unger (TU Dresden), Prof. Dr. Paul (GKSS Gestacht), as well as Dr. Fink, Dr. Loth and Prof. Dr. Schleicher (Fraunhofer Institute of Applied Polymer Research, Teltow-Seehof), the group of Dr. Dautzenberg (University of Potsdam), and also Dr. Rahn, R. Dicke, Dr. Heublein (Friedrich Schiller University of Jena). The authors greatly acknowledge the comprehensive assistance of S. Mebus and D. Stscherbina (Polymer Research Centre, Teltow-Seehof), of A. Horn and K. Muchina (Friedrich Schiller University, Jena) and of Helga Philipp in processing the manuskript of this book. The authors are pleased to acknowledge the always agreeable and stimulating cooperation with the publishers, especially with Dr. Ritterbusch and Dr. Anton from VCH.

List of Abbreviations for Volumes 1 and 2

Ac_2O	acetic acid anhydride
AGU	anhydroglucopyranose unit(s)
Bn	benzyl
Cadoxen	cadmiumethylenediamin chelate
CMC	carboxymethylcellulose
COSY	homonuclear chemical shift correlation spectroscopy
CP-MAS	cross-polarization magic angle spinning
CTA	cellulose triacetate
CTFA	cellulose trifluoroacetate
Cuam	cuprammonium hydroxide $[Cu(NH_3)_4]OH$
Cuen	cupriethylenediamine chelate
DMA	*N*,*N*-dimethylacetamide
DMAP	*N*,*N*-dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
DP	degree of polymerization
DP_n	number-average degree of polymerization
DP_v	viscosity-average degree of polymerization
DP_w	weight average degree of polymerization
DS	degree of substitution
DS_{Ac}	degree of substitution of acetyl groups
DS_{Cl}	degree of substitution of chlorine atoms
DS_{HPLC}	degree of substitution determined by means of HPLC
DS_N	degree of substitution of nitrogen atoms
DS_P	degree of substitution of phosphorus atoms
DS_S	degree of substitution of sulfur atoms
DS_{Si}	degree of substitution of silyl groups
DS_x	degree of substitution of xanthogenate groups
DTA	differential thermal analysis
DVS	divinyl sulfone
EDA	electron donor–acceptor
Et	ethyl
FeTNa	ferric sodium tartrate
FT	Fourier transform
GPC	gel-permeation chromatography
g-t	*gauche–trans*
GuOH	guanidinium hydroxide

H-CMC	the free acid of carboxymethylcellulose
HEC	hydroxyethylcellulose
HMPT	hexamethylphosphoric acid triamide
HPC	hydroxypropylcellulose
LB	Langmuir–Blodgett
LODP	level-off degree of polymerization
LRV	liquid retention value
M.W.	molecular weight
mesylate	methylsulfonate
Me	methyl
MF	mole fraction
MS	molar substitution
Nioxam	nickel ammonium hydroxide
Nioxen	nickel ethylenediamine chelate
NMMNO	*N*-methylmorpholine-*N*-oxide
NMP	*N*-methylpyrrolidone
r.h.	relative humidity
rt	room temperature
s (index)	substituted
SAXS	small-angle X-ray scattering
SEC	size-exclusion chromatography
SEM	scanning electron microscopy
SERS	Surface enhanced Raman spectroscopy
TDMS cellulose	thexyldimethylsilyl cellulose
TDMSCl	thexyldimethylchlorosilane
TEA	triethylamine
TEM	transmission electron microscopy
TG	thermogravimetry
t-g	*trans–gauche*
THF	tetrahydrofuran
TMS	trimethylsilyl
TMS-Cl	trimethylsilyl chloride
TPC	triphenylcarbinol
triflat	trifluoromethanesulfonate
WAXS	wide-angle X-ray scattering
WRV	water retention value
´ (index)	neighbour C-atom

1 Introduction

Cellulose, a linear 1,4-β-glucan, is the most abundant polymer available today worldwide. It is produced by nature at an annual rate of 10^{11}–10^{12} t, partially in a rather pure form, as for example in the seed hairs of the cotton plant, but mostly combined with lignin and with other polysaccharides, so-called 'hemicelluloses' in the cell wall of woody plants. The latter source comprises predominantly soft woods and hard woods from the forest and to some extent also stalks of annual plants like wheat straw or bamboo. As a further source, which up to now is just of scientific interest, bacterial cellulose has to be mentioned, produced extracellularly by e.g. *Acetobacter xylinum* strains.

The cellulose from woody plants has been isolated by large-scale chemical digestion processes for more than a century, dissolving the lignin and the hemicelluloses via a combined chemical transformation and cleavage, and leaving the cellulose component as a solid in a somewhat degraded state. Delignification of wood is usually performed as a multi-step process, increasing stepwise the specificity of interaction with the components to be dissolved. The whole process comprises a so-called digestion, removing most of the lignin as lignosulfonic acid (sulfite process) or as alkali or thiolignin (graft and sulfate process respectively), and subsequent bleaching steps for eliminating nearly all of the residual lignin (Fig. 1.1).

Purity and average chain length of the wood pulp obtained are controlled by the parameters of the digestion and bleaching steps, and have to be adapted to the end-use intended. Special purity requirements have to be met frequently for dissolving pulps, i.e. products employed for subsequent chemical conversion.

Cellulose as a polymer raw material is used for two general purposes: for many centuries it has served mankind as a polymer construction material, mainly in the form of intact wood but also in the form of natural textile fibers like cotton or flax, or in the form of paper and board. On the other hand, cellulose is a versatile starting material for subsequent chemical conversion, aiming at the production of artificial cellulose-based threads and films as well as of a variety of stable soluble cellulose derivatives to be used in many areas of industry and domestic life.

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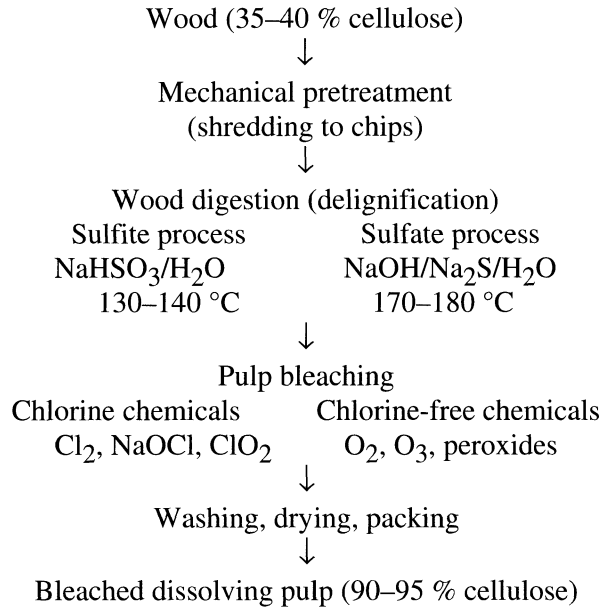

Figure 1.1. Delignification of wood

The chemical reactions taking place at the cellulose macromolecule, i.e. etherification and esterification, oxidation, and also grafting and crosslinking, but also chain degradation by various mechanisms, are the subject of cellulose chemistry. They will be the topic of this book mainly from the viewpoint of organic chemistry, but including also the necessary presentation of analytical procedures employed for characterizing the course of reaction and the structure of the reaction products.

Before going into some details on the scope of this book and its topical structure, a brief abridgment of the history of cellulose chemistry, as well as of recent inputs from general polymer chemistry and from saccharide chemistry seems to be appropriate. Empirical knowledge of dyeing cellulosic fibers, of burning wood and the preparation of charcoal, as well as of the biodegradation of cellulose by rotting, was acquired already thousands of years ago. The origin of the organic chemistry of cellulose can be traced back to the middle of the 19th century. This development was stimulated not only by scientific curiosity during this boom of experimental chemistry, but also by the more practical intention to get the water-insoluble cellulose into the dissolved state by a suitable chemical transformation for the purpose of preparing an artificial silk, i.e. an endless cellulose thread not available in nature (Klare, 1985). Milestones along this pathway were the discovery of cellulose nitrate by Schönbein in 1848, the preparation of Schweizers reagent, i.e. a cuprammonium hydroxide solution represent-

ing the first cellulose solvent in 1857, and the synthesis of an organo-soluble cellulose acetate by Schützenberger in 1865. The synthesis of cellulose nitrate formed the basis for the first industrial process of manufacturing 'artificial silk' by spinning a cellulose nitrate in acetic acid or in ethanol/diethyl ether into a precipitation bath of cold ethanol (wet spin process) or into an air stream for solvent evaporation (dry spin process), respectively, followed by denitration of the threads obtained with an aqueous solution of NaHS or $NH_4(HS)$. Moreover, cellulose nitrate was the basis of the first thermoplastic material mixed with campher as softener. Despite a remaining inflammability due to incomplete denitration the 'Chardonnet silk' was manufactured at a declining rate until world war II, but more successful competitors arose already at the end of the previous century. Regenerated cellulose filaments free of the hazard of inflammability were obtained by spinning a cellulose solution in cuprammonium hydroxide into an aqueous bath. The development of the 'viscose route' to artificial silk to a large-scale process was definitely promoted by the commercial availability of sulfite softwood pulp at the same time. The manufacture of the above mentioned cellulose esters on a technical scale already at the end of the last century, as well as the production of water-soluble methyl and carboxymethylcellulose at the beginning of this century were achieved on the basis of classical organic chemistry without taking into account the macromolecular character of the polymer.

By far the largest part of the cellulose-based artificial fibers have been manufactured for about the last century by the so-called viscose process, invented in 1892 by Cross, Bevan and Beadle (Cross et al., 1893). This process is practised today with an output of about 3 million tons annually worldwide. It makes use of the formation of cellulose xanthogenate, i.e. a water-soluble unstable anionic ester prepared by reacting cellulose with CS_2 and sodium hydroxide and decomposed by spinning in an acid bath.

The origin of cellulose chemistry as a branch of polymer chemistry can be traced back to the fundamental experiments of Hermann Staudinger in the 1920s and 1930s on acetylation and deacetylation of cellulose, resulting in the concept of polymer-analogous reactions (Staudinger and Daumiller, 1937). According to this concept, functional groups of macromolecules can undergo the same kinds of reactions as the appropriate analogous monomer compounds, and under favorable conditions these polymer-analogous reactions, e.g. acetylation and deacetylation of cellulose, can be performed without significant degradation of the polymer chains. It was further observed by Staudinger that the supramolecular structure of the polymer can play an important role in determining the rate and the final degree of conversion in reactions of this kind.

Application of the continuously expanding knowledge on the course and the mechanism of polymer-analogous reactions to cellulose subsequently proceeded along three routes: the first one consisted in a thorough investigation of reactions or reaction sequences already practised in large-scale technical processes from

the viewpoint of macromolecular science, taking into account e.g. problems of chain degradation, as well as of side reactions. A classical example is the research on the viscose process between the 1940s and the 1960s with its decisive consequences to the general level of fiber quality and the diversification of fiber properties. As a second route, the systematic application of principles elaborated with synthetic polymers to cellulose, like grafting or crosslinking, has to be mentioned. The third route is closely related to the name of Z.A. Rogowin (Rogowin and Galbraich, 1983), who systematically realized the principle of adequate reactivity of monomers and polymers to cellulose by performing a host of reactions and reaction sequences to the anhydroglucose units of cellulose, thereby arriving many new reaction principles of cellulose chemistry and a lot of new cellulose derivatives.

A new area in cellulose chemistry was started about 30 years ago by the discovery of many new non-aqueous solvent systems for cellulose including numerous aprotic ones (Philipp, 1990). These new solvent systems paved the way to a systematic investigation of homogeneous reactions of cellulose so far having been performed under severely limited conditions only. On the other hand, some of these new solvent systems offered promising alternatives to the well-established but still ecologically problematic viscose process. Overviewing the present state of knowledge, it can be concluded that the organic chemistry of cellulose, as well as its chemical technology, received a strong impetus from these new solvent systems by opening up a pathway to really new and well-defined cellulose products and by enlarging our knowledge on interaction of the cellulose molecule with liquid systems.

During the same period of time, cellulose chemistry and general saccharide chemistry came closer together by an exchange of ideas and of experimental techniques. First of all this holds true with regard to regioselectivity of reaction, which has been realized for many years in sugar chemistry along well-known routes, but which represented a rather new approach in cellulose chemistry, definitely promoted by the availability of the non-aqueous solvent systems as media for homogeneous cellulose derivatization. The input of sugar chemistry comprised new routes of synthesis, as well as new approaches to characterization by instrumental techniques, including the supply of low molecular model compounds, for example regioselectively substituted glucoses. Regarding the techniques of instrumental analysis, high-resolution liquid NMR spectroscopy and modern chromatographic techniques shall be explicitly mentioned here. On the other hand, promising new achievements in the organic chemistry of cellulose promoted a broadening of the scope of the whole area by including other polysaccharides chemically related to cellulose, like amylose chitosan, or xylan, into research on synthesis and characterization of new products.

The present 'state of the art' in cellulose chemistry can be summarized as follows: first of all, the efforts for synthesis of new, hitherto unknown cellulose

derivatives have to be mentioned here. This comprises the introduction of new substituents and new functionalized side chains with the close control of substitution site within the anhydroglucose unit, and also a close control of chain degradation. This work is supplemented by development or adaptation of suitable analytical procedures, and by interdisciplinary studies on the effects of selective site substitution on the physical properties and the biological activities of the compounds obtained. The present boom of supramolecular chemistry, aimed at the deliberate construction of well-ordered aggregates of low molecular or macromolecular entities opens up new routes to advance cellulose materials. As already realized examples the numerous cellulose-based liquid-crystalline systems and ordered mono- and multilayers can be cited here (compare Guo and Gray, 1994).

The current development in the area of commercially produced esters and ethers of cellulose is characterized by a continuous process optimization and a still better adaptation of the products obtained to specific and new end-uses. This is at least partially achieved by a deeper understanding of the course and mechanism of reaction and of relations between conditions of synthesis, product structure, and product properties. Special emphasis is given today to ecological requirements by minimizing the input of chemicals via a better control of side reactions, by avoiding hazardous process components, and by developing really safe techniques of recycling and/or waste disposal. Also the biodegradability of cellulosic compounds receives increasing attention in research and development.

The search for an alternative route to artificial cellulose threads employing organic solvent systems including NMMNO (see chapter 2.2.2), is acting as an important stimulus to today's cellulose research. These recent developments in the manmade fiber area, including those in the viscose process of better ecocompatibility represent a striking example of the mutual exchange and the growing co-operation between academic and industrial research.

Considering briefly now the scope of this book and its topical structure, its two volumes are centered on the organic chemistry of cellulose, but consider adequately also problems of supramolecular structure. The main topics are the routes, the mechanisms, and the kinetics of derivatization reactions at the macromolecular level of cellulose, and their interpretation on the basis of today's organic chemistry. Special consideration is given to the site selectivity of cellulose derivatization in dependence on reaction conditions and on the interaction between derivatization and chain degradation. Besides these more fundamental aspects, the book intends to convey to the reader the practical experience acquired by the authors' groups, including sample pretreatment, isolation, and purification of reaction products, as well as analytical procedures for characterizing the course of reaction and the products obtained.

The book offers itself as a text book for graduate students with a good background in organic and macromolecular chemistry, but also to professional peo-

ple, i.e. chemists, physicists, biologists, and engineers active in chemical processing of cellulose. As a monograph it yields information on routes to cellulose derivatives, on the structure of the reaction products, as well as on the experimental procedures already successfully practised. Although a detailed description of large-scale processes of cellulose derivatization is outside the framework of this book, the chemical engineer will find some information connecting reaction routes and reaction principles with their large-scale realization.

In order to cope adequately with these claims, the book is divided into two volumes. The first volume contains information on a more general nature of cellulose structure and properties and their changes on activation, swelling, and dissolution, as well as on some principles of cellulose reactions and cellulose degradation. A rather detailed survey of the analytical techniques for characterizing the molecular, supramolecular, and morphological structure of cellulosic compounds is also included in this first volume, emphasizing the close correlation between progress in the synthesis of new cellulosic compounds and structures on the one hand, and the development and adaptation of adequate analytical techniques on the other. The second volume deals with the various classes of cellulose derivatives systematized according to principles of organic polymer chemistry and considering adequately the achievements of reaction theory and its application to cellulose derivatization. The volume starts with an outline of the *in vivo* and *in vitro* synthesis of cellulose, and of routes to changes of the polymer skeleton of this polysaccharide. Subsequently two areas of cellulose chemistry rather neglected in the previous decennaries, i.e. the interaction of cellulose with basic compounds and metal complex formation with cellulosic hydroxy groups as ligands, are treated in some detail from the present point of view, before turning then to the classical areas of cellulose derivatization i.e. esterification, etherification, and oxidation. The volume is finalized by an outlook presenting problems and trends in cellulose chemistry in the foreseeable future and emphasizing a close co-operation between various areas of science, as well as between fundamental and applied research as a prerequisite for future success. As a special feature of the book, a separate chapter with laboratory procedures for cellulose derivatization and analysis proven in the authors' groups is included at the end of each volume.

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2 General Considerations on Structure and Reactivity of Cellulose

2.1 Structure and Properties of Cellulose

The structure of cellulose, although one of the most unique and simple in the field of polysaccharides, has a rather remarkable and complex influence on the course of chemical reactions of this polymer. Moreover, the structure is responsible for the macroscopic properties of the polymer, which will be considered briefly in the final subsection (2.1.7.4) stressing the properties relevant for chemical transformation.

For the purposes of a clear, systematic description of the complex structure of cellulose, it is generally considered adequate to discern three structural levels, i.e. (i) the molecular level of the single macromolecule; (ii) the supramolecular level of packing and mutual ordering of the macromolecules; (iii) the morphological level concerning the architecture of already rather complex structural entities, as well as the corresponding pore system.

Besides these three levels of structure of cellulose, the presence of alien, low and high molecular compounds associated with cellulose macromolecules has to be considered. A review (O'Sullivan, 1997) emphasizes the complexity of the physical structure of cellulose, the relation of this structure to the route of biosynthesis of this polymer, and the progress achieved by computer modelling in understanding this studies.

All the sections of this chapter include brief comments on the analytical techniques employed for assessing the structural parameters in question.

2.1.1 The molecular structure

Cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucopyranose units (AGU), which are linked together by β-(1→4)-glycosidic bonds. Taking the dimer cellobiose as the basic unit, cellulose can be considered as an isotactic polymer of cellobiose (Fig. 2.1.1). D-Glucose can be recovered from cellulose with a nearly quantitative yield after a suitable hydrolytic treatment with aqueous acid. Each of the AGUs possesses hydroxy groups at C-2, C-3, and C-6 positions, capable of undergoing the typical reactions known for primary

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and secondary alcohols. The vicinal secondary hydroxy groups represent a typical glycol structure. The hydroxy groups at both ends of the cellulose chain show different behavior. The C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxy group is nonreducing. The bridging and the ring oxygen atom are predominantely involved in intra- and intermolecular interactions, mainly hydrogen bonds, and in degradation reactions.

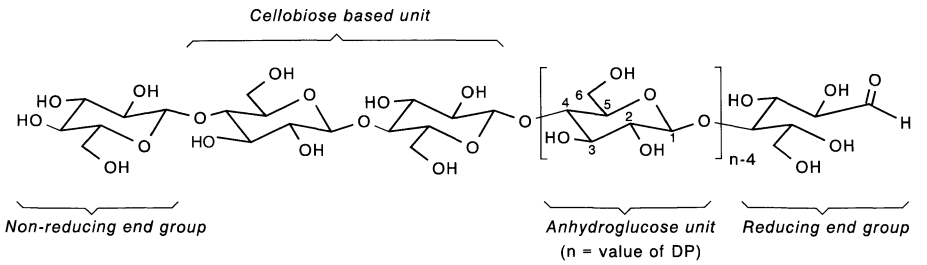

Figure 2.1.1. Molecular structure of cellulose.

The conformation of the AGU in the cellulose chain is generally assumed to be a $^4C_1$ chair conformation, as derived from X-ray diffraction and NMR measurements with β-D-glucose as shown in Fig. 2.1.2. In this conformation the free hydroxy groups are positioned in the ring plane (equatorial), while the hydrogen atoms are in a vertical position (axial).

Table 2.1.1. Assignment of the ^{13}C NMR signals of unsubstituted cellulose (cellulose of *DP* (degree of polymerization) = 40 in NaOH/D_2O)

C-atom	Assignment (ppm)
C-1	104.5
C-2	74.7
C-3	76.1
C-4	79.8
C-5	76.3
C-6	61.5

On transition from the monomer 'glucose' to the polymer 'cellulose', the water solubility decreases already above a *DP* of 6, due to strong intermolecular interaction via hydrogen bonds and a glucan of *DP* 30 already represents the polymer 'cellulose' in its structure and properties. The transition from the monomer to the polymer is reflected also by the ^{13}C NMR spectra depicted in Fig. 2.1.2, with that of cellohexaose. The last one is already closely resembling that of cel-

lulose and showing no signal splitting due to equilibrium of the α- and β-anomers clearly visible in the spectra of glucose and cellobiose (Nehls et al., 1994). The ^{13}C NMR solution spectrum of unsubstituted cellulose consists of six signals corresponding to the six C-atoms of the anhydroglucose unit (AGU), with the assignment listed in Table 2.1.1, to which the reader will be frequently referred throughout this book.

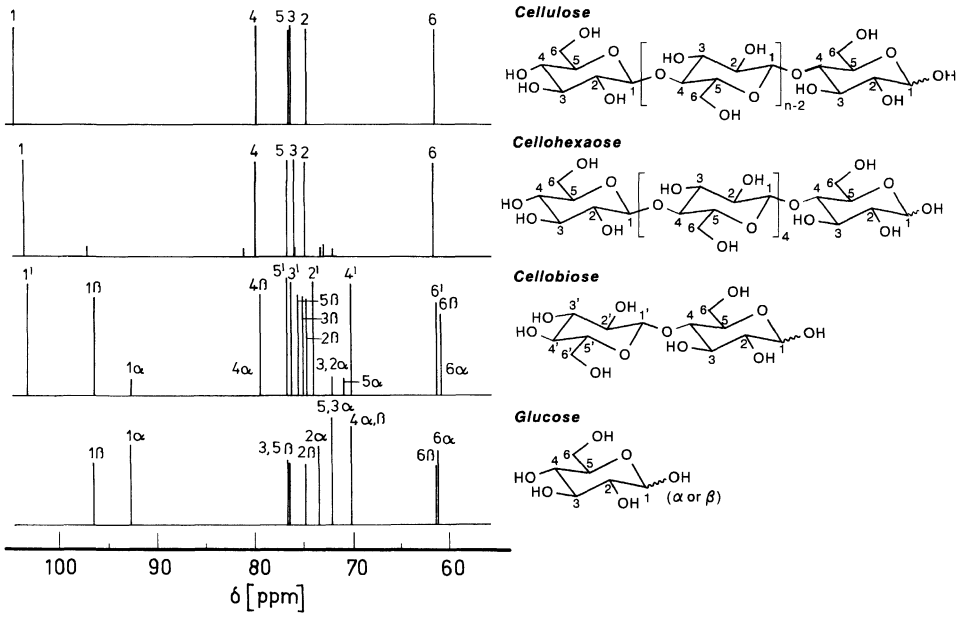

Figure 2.1.2. ^{13}C NMR spectra of glucose, oligoglucose, and cellulose (Nehls et al., 1994).

Deviations from this ideal structure outlined above are usually observed in technical cellulose samples like bleached cotton or wood pulp, due to the presence of carboxylic acid groups and also some carbonyl groups. The rather wide range of carboxyl contents in technical cellulose materials is illustrated in Table 2.1.2. The amount of carboxyl groups is usually assessed by titration of the acid form or by an ion-exchange process with a suitable cation (cf. chapter 3).

The molecular size of cellulose can be defined by its average degree of polymerization (*DP*). The average molecular mass results from the product of the *DP* and the molecular mass of the repeating AGU. The *DP* values of cellulose samples differ widely, depending on origin and pretreatment. *DP* values of several types of native and regenerated cellulose are presented in Table 2.1.3.

Table 2.1.2. Content of carboxylic acid and carbonyl groups in some specimens of native cellulose (Schleicher and Lang, 1994)

Specimen	mmol of acid groups/kg	mmol of carbonyl groups/kg
Cotton linters	<10	–
Sulfite-dissolving pulp	20–30	7–20
Prehydrolyzed sulfate pulp	8–30	2–5
Paper pulp	20–300	–

Table 2.1.3. *DP* range of various cellulose materials

Material	Range of *DP*
Native cotton	up to 12000
Scoured and bleached cotton linters	800–1800
Wood pulp (dissolving pulp)	600–1200
Man-made cellulose filaments and fibers	250–500
Cellulose powders (prepared by partial hydrolysis and mechanical disintegration)	100–200

Cellulose isolated from native sources is always polydisperse, i.e. it consists of a mixture of macromolecules with widely differing chain lengths (Fig. 2.1.3). The determination of the *DP* is usually performed viscosimetrically after dissolving the sample in complexing aqueous solvents, like cuprammonium hydroxide (Cuam) or Cuen (see chapter 4.3). As is well known in macromolecular chemistry, besides the *DP*, as an average value, the chain length distribution is relevant to structure description and chemical reactions, even in technical processes. This chain length distribution can be influenced significantly by the procedure applied in isolation and pretreatment of the sample.

Besides a monomodal distribution, bimodal curves with a second peak have been reported, especially for dissolving pulps. The chain-length distribution is generally assessed after converting the cellulose to an organo-soluble nitrate or carbanilate under conditions of minimal chain degradation (see chapter 3.1).

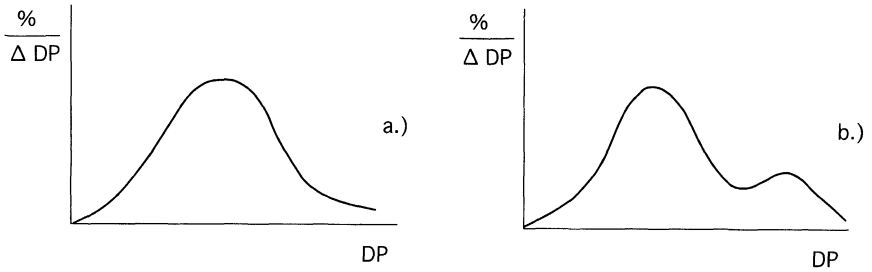

Figure 2.1.3. Chain-length distribution in a polymer sample: (a) unimodal; (b) bimodal.

The backbone conformation of the chain is determined by the bond angles and the bond length of the oxygen glycosidic bridge and by the torsion angles of this bridge (Fig. 2.1.4).

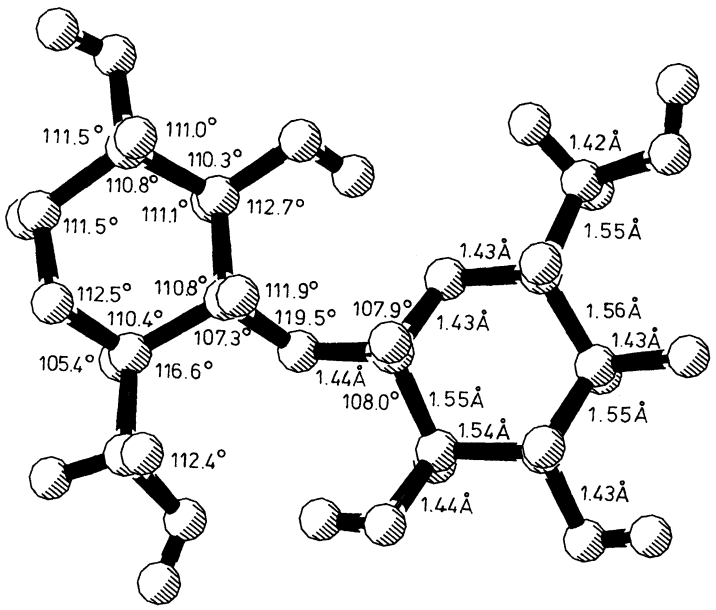

Figure 2.1.4. Structural data of the cellulose chain (calculated by Ganster, Teltow-Seehof, with the Polymer Consistent forcefield (PCFF) for cellulose I_β, Maple et al., 1994).

Generally a bent backbone conformation is assumed. According to present knowledge, the existence of a straight conformation can rather be excluded for native as well as for regenerated cellulose.

The C-6 conformation (CH_2OH group) is today assumed to be t-g (*trans–gauche*) for cellulose I, while for cellulose II a g-t as well as a 'mixed' conformation of g-t and t-g (Gardner and Blackwell, 1974) is discussed. From these findings important consequences do result for the intramolecular and the intermolecular hydrogen bond system of cellulose in the solid state (see next subchapter).

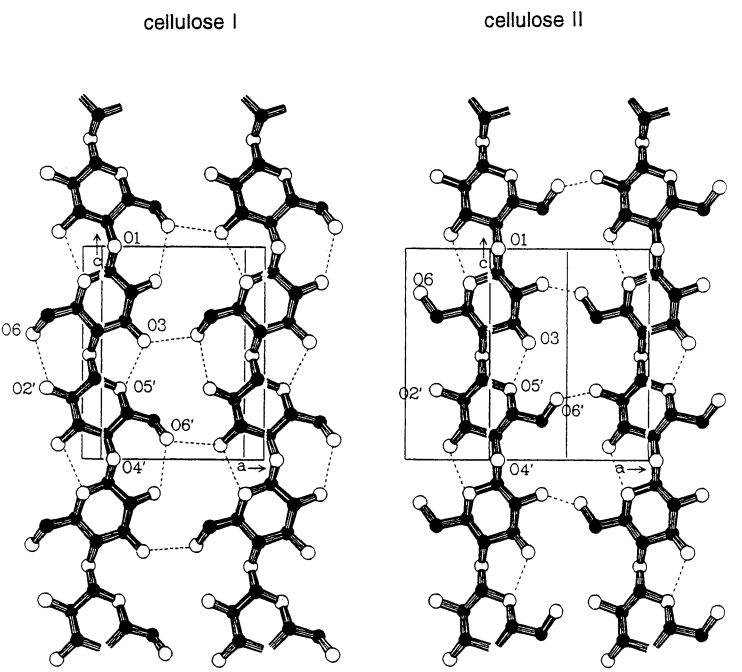

Figure 2.1.5. Most probable hydrogen bond patterns of cellulose allomorphs (Kroon-Batenburg et al., 1986).

The presence of intramolecular hydrogen bonds is of high relevance with regard to single-chain conformation. The existence of hydrogen bonds between O-3–H and O-5′, and between O-2–H and O-6′ in native crystalline cellulose can be concluded from X-ray diffraction, NMR-, and IR data. These intramolecular hydrogen bonds, depicted schematically in Fig. 2.1.5, are responsible for the considerable stiffness of the cellulose chain and stabilize the two-fold helix conformation of crystalline cellulose. This spatial chain conformation of crystalline cellulose I and II is adequately represented by a 1,2 helix (Zugenmaier, 1989; Gardner and Blackwell, 1974; Kolpak and Blackwell, 1976). Sometimes deviations from this two-fold helix due to alternate hydrogen-bond formation are discussed (Horii et al., 1987). Larger deviations from the two-fold helix are discussed for regions of low order in the cellulose solid state structure.

2.1.2 The supramolecular structure

As described before the cellulose chains have a strong tendency to aggregate to highly ordered structural entities due to their chemical constitution and their spatial conformation.

The molecular basis of this tendency to form ordered structures is an extended network of hydrogen bonds consisting of the above-mentioned intramolecular bonds, as well as of intermolecular bonds (see Fig. 2.1.5). The detailed structure of this hydrogen-bond network is still subject to discussion. Among the intermolecular hydrogen bonds, that between O-6–H and O-3 of another chain (O-3´´) is generally considered as the most important one for cellulose I from the chemical point of view. The intermolecular hydrogen bonds are the predominant factor responsible for interchain cohesion. This interchain cohesion is favored by the high spatial regularity of the hydrogen-bond forming sites and by the involvement of all three hydroxy groups in the hydrogen-bond network. The latter fact is of relevance in all heterogeneous reactions of cellulose and will be referred to rather frequently in later sections of this book.

As already indicated above, the order of the macromolecules in a cellulose fiber is not uniform throughout the whole structure, and we have to assume regions of low order as well as of very high crystalline order. In 1957, Marchessault and Howsmon proposed the model of a continuous-order spectrum of solid state cellulose, which at that time was found very interesting in connection with the accessibility of the hydroxy groups in heterogeneous cellulose reactions (Marchessault and Howsmon, 1957). This model, however, is abandoned today, as obviously regions of medium order play a minor role only, and the experimental evidence available today is adequately interpreted by a two-phase model assuming low ordered ('amorphous') and highly ordered ('crystalline') regions, and neglecting the rather small amount of matter with an intermediate state of order (Hearle, 1958). Also throughout this book a two-phase model with crystalline and amorphous regions (fringed fibril model) will be used in discussing the course of heterogeneous cellulose reactions (see Fig. 2.1.6).

The relative amount of polymer within the highly ordered regions, the so-called degree of crystallinity, is usually assessed from the wide-angle X-ray scattering (WAXS) pattern, and more recently also from the evaluation of the ^{13}C high-resolution cross-polarization magic angle spinning (CP-MAS) solid state NMR spectrum of the polymer. The degree of crystallinity of different cellulose samples covers a wide range and depends on origin and pretreatment of the sample (see Table 2.1.4).

Cellulose exists in several crystal modifications, differing in unit cell dimensions and, possibly, in chain polarity. Figure 2.1.7 summarizes some relevant crystallographic data.

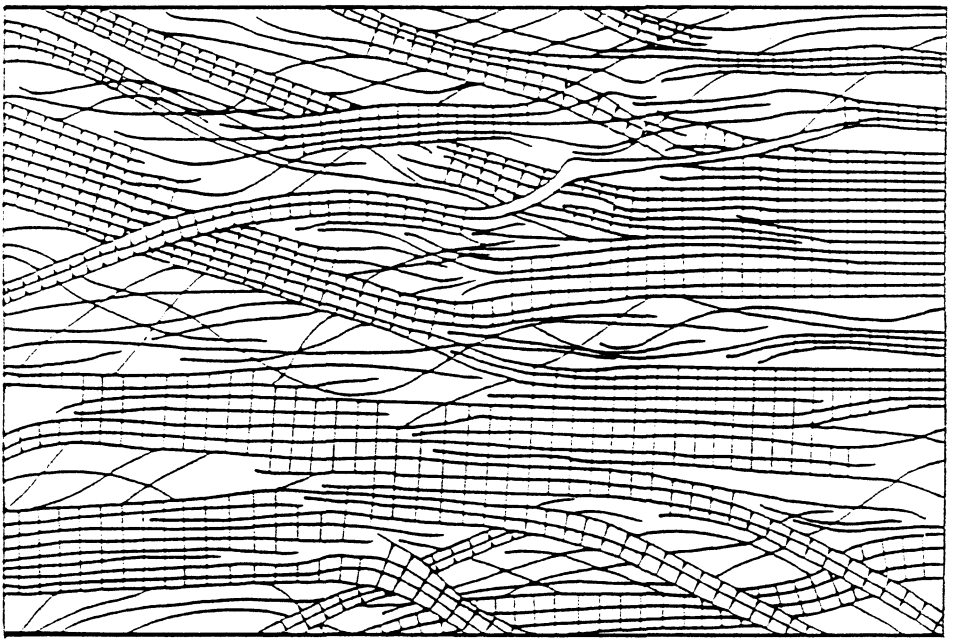

Figure 2.1.6. Fringed fibril model of cellulose supramolecular structure (Hearle, 1958).

Table 2.1.4. X-ray crystallinity $\bar{x}_C$ of some cellulose materials (Fink and Walenta, 1994)

Sample	Comments	$\bar{x}_C$ (%)
Cotton linters (scoured and bleached)	Samples of various origin	56–63
Sulfite dissolving pulp	Samples of various origin	50–56
Cellulose powder	Spruce sulfite pulp hydrolyzed	54
Sulfate pulp	Prehydrolyzed	46
Viscose rayon	Samples of various origin	27–40
Regenerated cellulose film	Samples of various origin	40–45
Experimental cellulose II filament	Filament spun from a solution of cellulose in *N*-methylmorpholine-*N*-oxide into water	42
Experimental cellulose II filament	Filament spun from trimethylsilyl cellulose solution into an acid bath	11

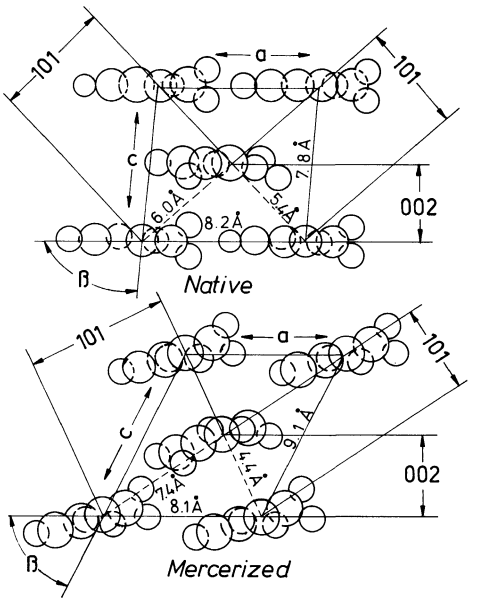

Figure 2.1.7. Some lattice plane distances of cellulose I (native) and cellulose II (mercerized) relevant for chemical modification (Krässig, 1993). Lattice plain notations according to Meyer, Mark, and Misch.

For crystalline native cellulose, i.e. cellulose I, Meyer, Mark and Misch (Meyer and Mark, 1929; Meyer and Misch, 1937) proposed a unit cell of the crystal lattice according to Fig. 2.1.8 already about 60 years ago, which is still applicable for practical purpose today. This model assumes a monoclinic unit cell with the space group $P2_1$ with two antiparallel cellobiose chain segments running in opposite directions along the fiber axis.

The dimensions of this cell are given in Table 2.1.5. Honjo and Watanabe (1958) concluded from their low-temperature X-ray measurements the doubling of the parameters *a* and *c* and arrived at an eight-chain unit cell.

Table 2.1.5. Unit cell dimensions of various cellulose allomorphs (as accomplished by Krässig, 1993)

a-axis (Å)	*b*-axis (Å)	*c*-axis (Å)	γ (deg)[a]	Polymorph
7.85	8.17	10.34	96.4	cellulose I
9.08	7.92	10.34	117.3	cellulose II
9.9	7.74	10.3	122	cellulose III
7.9	8.11	10.3	90	cellulose IV

[a] γ = lattice angle

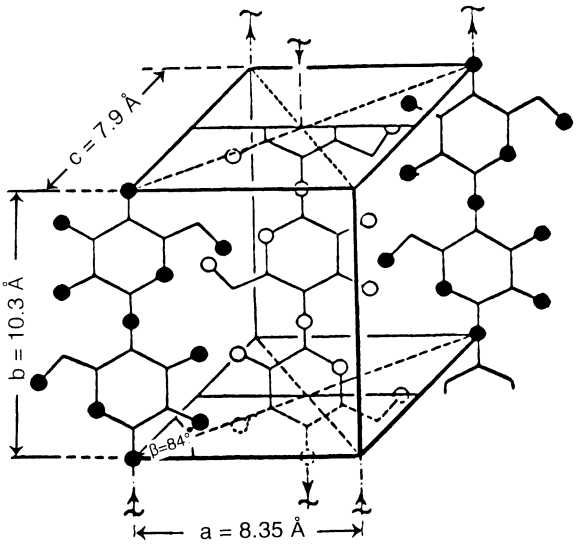

Figure 2.1.8. Unit cell of cellulose I according to the Meyer–Misch model.

Sarko and Muggli (1974) agree to this eight-chain unit cell, but state that also the Meyer–Misch model adequately represents most of the crystallographic evidence of native crystalline cellulose. Based on a more refined WAXS technique, Gardner and Blackwell (1974) proposed for cellulose (from *valonia algae*) a monoclinic lattice with two parallel running chains, and assume this to be valid for cellulose I in general. Sarko and Muggli (1974) proposed from a combined packing and X-ray pattern intensity analysis a triclinic lattice cell with two cellulose chain segments running parallel along the fiber axis. From an evaluation of high-resolution solid state ^{13}C NMR data VanderHart and Atalla (1984) concluded about 10 years ago that crystalline native cellulose is a mixture of two crystalline modifications, i.e. of I_α and I_β cellulose (Atalla and VanderHart, 1984; VanderHart and Atalla, 1984). According to these authors, bacterial and valonia cellulose contain a large amount of I_α modification, whereas in ramie cotton or wood cellulose the I_β phase is the dominating modification. Sugijama et al. (1991) described, on the basis of electron diffraction experiments, the I_α phase as a triclinic P-1 structure, with one cellulose chain per unit cell, and assumed for the I_β modification a monoclinic unit cell of the Meyer–Misch type (space group P-2_1 with two chains per unit cell). According to Yamamoto and Horii (1993) the I_α phase is metastable and can be transformed by annealing into the thermodynamically more stable I_β phase.

Besides cellulose I, the crystalline modification of cellulose II is the most important from a technical and commercial point of view. It is formed by precipitating cellulose from solution into an aqueous medium at room or slightly

elevated temperature, i.e. in technical spinning processes for man-made cellulose fibers. It is also obtained in the large-scale mercerization process of cotton, which proceeds via the formation of sodium cellulose by interaction of the polymer with aqueous sodium hydroxide and subsequent decomposition of this intermediate by neutralization or washing out of the sodium hydroxide. The process of transformation of cellulose I to cellulose II is generally considered today as irreversible, although according to Fink and Philipp (1985) sodium cellulose can partially be retransformed to cellulose I.

According to Andress (1929) the crystal structure of cellulose II is represented by a monoclinic unit cell with the space group P-2_1, consisting of two antiparallel running cellulose chain segments that form a 2/1 helix. The average lattice data generally accepted today were proposed by Kolpak and Blackwell (1976) and are listed in Table 2.1.5.

The hydrogen bond system of cellulose II appears to be more complicated than that of cellulose I and results in an higher intermolecular crosslinking density. According to Kolpak and Blackwell (1976), intermolecular hydrogen bonds are formed in cellulose I by 'linking' neighboring chains along the *a*-axis by an intermolecular hydrogen bond O-6···H-O(3), so that the chains form hydrogen bonded sheets of chains parallel to the *a*-axis, which means in the 020 plane. For cellulose II, Blackwell and Kolpak (1978) state that the $-CH_2OH$ groups are in the t-g position in the case of the center chain forming sheets very similar to those in native cellulose. Each chain forms two intramolecular center bonds and is linked by an intermolecular O-6···HO-3 bond to the next chain along the *a*-axis. In the case of the corner chain, however, the CH_2OH groups are in the g-t position. Each chain has the O-3···HO-5′ intramolecular bond but forms two intermolecular bonds, i.e. O-6···HO-2 to the next chain along the *a*-axis in the 020 plane, and OH-2···O-2′ to the chain along the diagonal in the 110 plane (index ′ means atom of the next AGU).

The crystalline modification, cellulose III, is obtained by treating celluloses I or II with liquid ammonia below –30 °C and subsequently recrystallizing the sample by evaporation of the ammonia. Small differences in lattice dimensions obviously exist between the two submodifications cellulose III_I and III_{II}.

As a fourth modification, cellulose IV may be mentioned briefly, which is formed on treating the other modifications in a suitable liquid at high temperature under tension, the average lattice data being listed in Table 2.1.5.

In all the four crystalline modifications of cellulose the repeating unit of the lattice cell along the fiber axis amounts to 1.03 nm. In contrast with this generally accepted repeating distance along the fiber axis, the polarity of the glucan chains along this axis, i.e. the mutual position of their reducing end groups, is still somewhat a question of discussion. For cellulose II, an antiparallel position of the chain packing, backed by strong experimental evidence, is mostly accepted. For cellulose I, the original Meyer–Misch model also proposed an anti-

parallel position, but on the basis of more refined results Gardner and Blackwell suggested, in 1974, a unit cell model with parallel chains which was subsequently agreed to by numerous groups. Pertsin et al. (1984, 1986), on the other hand, arrived at the conclusion that from these potential energy calculations no decision can be made on the parallel or antiparallel chain packing in cellulose I. In favor of antiparallel packing mode, often the reasoning is used that the transition from cellulose I to cellulose II takes place in the solid state without complete lost of crystalline order.

Although recently results relevant to further progress were achieved by some other methods like high-resolution solid state NMR spectroscopy or electron microscopy, the main source of information on the crystalline regions of cellulose is still the wide angle scattering technique. Besides the degree of crystallinity (see Table 2.1.4), the WAXS pattern yields information on the size and perfection of the crystalline domains via a detailed analysis of the reflex profiles (Hofmann et al., 1989). Table 2.1.6 summarizes some data obtained with different cellulose samples of cellulose crystalline modifications I and II.

As can be seen from the data for cotton linters and wood dissolving pulp, the anisometry of the crystallites, i.e. the ratio of length to width is rather low. Crystallite width decreases in the order valonia > cotton linters > wood pulp > viscose rayon and the same ranking obviously holds true for the perfection of crystallite order, as demonstrated by the increase of the disorder parameter.

Information available today on the structure of the so-called amorphous regions in cellulose materials is still rather scarce. An irregular packing of the cellulose chains with stiff chain segments of about 0.5 nm diameter from X-ray scattering evaluation was assumed (Ellefsen et al., 1957). According to Paakari et al. (1989) the length of these stiff segments amounts to about one cellobiose unit, and a back folding of the chains with a wide back-folding radius cannot be excluded. Paakari assumes a 'nanocrystalline' structure in the amorphous regions, with widened, irregular polymer helixes. Also Pizzi and Eaton (1985) mention this irregular helical structure, with strong deviations from the 2/1 helix. From high-resolution solid state ^{13}C NMR spectra, irregularities in the helical structure of the chains in the amorphous phase due to a complete breaking of the intermolecular and a partial breaking of the intramolecular hydrogen bonds was concluded (Horii et al., 1987). Fink et al. (1987) investigated different amorphous samples (ball-milled cellulose I and II, a saponified cellulose acetate) by analyzing the WAXS radial distribution curve of scattering intensity and found small differences only between these three samples. The above authors assume an irregular sequence of straight-chain segments with possibly a bent and twisted conformation.

Table 2.1.6. Size and degree of disorder of crystallites of cellulose I and II (Fink and Walenta, 1994)

Sample	Allomorph	Average crystallite size		Area of cross section (nm^3)	Disorder parameter[c] $\sqrt{e^2}$
		Crystallite length (nm)[a]	Crystallite width (nm)[b]		
Valonia cellulose	I	–	8.9–10.1	–	0.01–0.02
Cotton linters	I	8.5–10.0	4.7–6.0	33–36	0.012–0.07
Sulfite dissolving pulp	I	7.5–9.7	4.1–4.7	16–21	–
Mercerized linters	II	–	5.9	–	0.027
Viscose rayon	II	–	4.2	–	0.032
Viscose staple	II	–	3.9	–	0.034

[a]Crystallite length calculated from 040 WAXS peak.
[b]Crystallite width calculated by Scherrer calculation (Klug and Alexander, 1974).
[c]Calculated according to (Hofmann and Walenta, 1987).

As already mentioned the supramolecular structure of cellulose is adequately represented by a two-phase model based on polymer chain aggregation to fibrillar structures. This smallest fibril structural unit, the microfibril (Rånby, 1954; Frey-Wyssting, 1954), can be considered simultaneously as the most complex entity of the supramolecular structural level and as the basic unit of the morphological structure. Its inner architecture will be considered here deliberately in connection with the supramolecular level. Regarding the mutual positioning of crystalline and amorphous regions within the fibrillar entities, three principle models have been discussed so far, i.e.

(i) a micellar model with interfibrillar chain segments forming the amorphous regions,

(ii) the string model with fibrils of equal diameter containing the amorphous regions at the fibril surface or in the form of dislocations within the crystallites, and

(iii) a back-folding model with the amorphous regions being formed by the back-folding section of the glucan chains, resulting in an antiparallel polarity of the chains.

According to present knowledge, this string model and the back-folding model are rather far from reality, as for example no long period reflexes could be observed in the small-angle X-ray diagram of native cellulose. The original micellar model was further elaborated in the 1950s by Hearle to a fringe fibrillar model (Hearle, 1958), which is supported by recent WAXS and ^{13}C CP-MAS NMR results. From WAXS results obtained with cellulose samples widely differing in physical structure, it is concluded that a non-uniform fringe fibrillar structure with ordered and disordered regions differing in size and perfection of the crystallites, comes rather close to reality. The fringe fibrillar model depicted schematically already in Fig. 2.1.6 obviously is the appropriate one for understanding the structure of cellulose at the borderline between the supramolecular and the morphological level, and its changes during cellulose reactions. It will therefore be employed throughout this book in discussing relations between the structure and the chemical reactivity of cellulose.

2.1.3 The morphological structure

Cellulose morphology can be understood as a well-organized architecture of fibrillar elements. In native celluloses we find a hierarchy of fibrillar entities, usually organized in layers differing in fibrillar texture. The morphology of regenerated cellulose fibers and films is generally characterized by fibrillar networks differing in tightness. Rather often a skin-core structure is typical for the morphology of these regenerated cellulose products (Fig. 2.1.9).

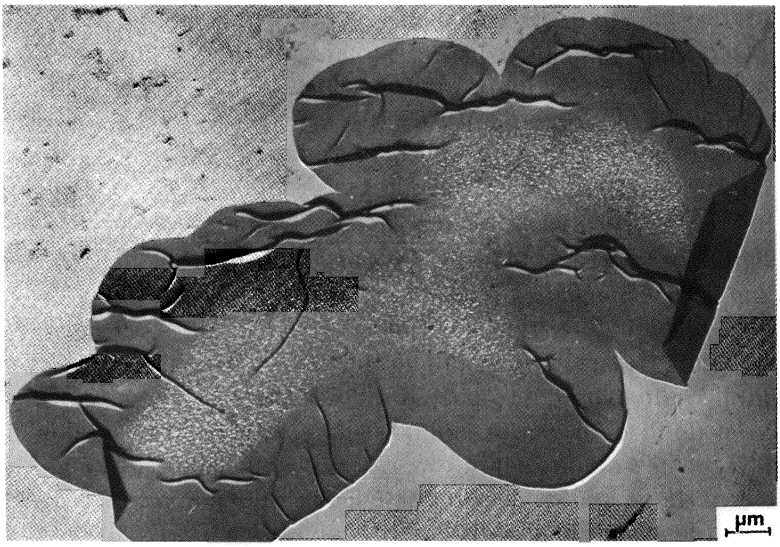

Figure 2.1.9. Skin-core morphology of viscose rayon cord (micrograph H.-J. Purz, Fraunhofer Institute of Applied Polymer Research, Teltow-Seehof).

As predominantly native cellulose is used as a starting material for chemical conversion the following considerations on cellulose morphology will be limited to the native structure.

Information on cellulose morphology is acquired today mainly by electron microscopic techniques (scanning and transmission electron microscopy), but also light microscopy exclusively employed in the first part of this century, is still an indispensable tool in the investigation of the gross morphology.

By several authors, the so-called elementary fibril has been considered as the smallest morphological unit (Mühlethaler, 1965; Heyn, 1966). A uniform elementary fibril of about 3.5 nm in diameter is sometimes assumed (Fengel and Wegener, 1989). But this seems questionable with regard to recent electron microscopic investigations (Chanzy et al., 1986), WAXS data, and transmission electron microscopy data (Fink et al., 1990). A non-uniformity of diameter in the range 3–20 nm, depending on the cellulose source, can be considered more probable.

From the authors' point of view, the microfibril is the lowest well-defined morphological entity, although it consists of non-uniform subunits. The microfibrils aggregate to larger morphological entities with diameters in the range 10–50 nm (Fink et al., 1990; Fig. 2.1.10), and significantly depending on the cellulose origin (Table 2.1.7). The length of the microfibrils can reach micrometers. For macrofibrils as aggregates of microfibrils, diameters in the micrometer range are reported (Fengel and Wegener, 1989; Krässig, 1993).

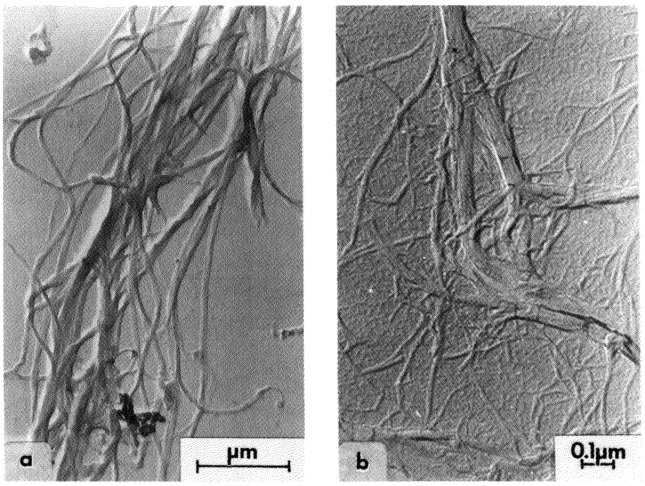

Figure 2.1.10. Isolated microfibrils of cellulose of different origin (a) cotton linters, (b) spruce sulfite pulp (Fink et al., 1990).

Table 2.1.7. Range of microfibril diameters of various cellulose samples (Fink et al, 1990)

Sample	Microfibril diameter (nm)
Bacterial cellulose	4–7
Cotton linters	7–9
Ramie	10–15
Dissolving pulp	10–30
Valonia cellulose	10–35

Micro- and macrofibrils represent the construction units of the cellulose fiber cell-wall architecture. This cell-wall morphology is characterized by layers differing in fibril texture, as shown schematically in Fig. 2.1.11 for a cotton fiber and a delignified spruce pulp fiber.

Despite the different origin and function of these fiber cells, some general similarities of morphological architecture can be recognized. Both fibers consist of different layers with the fibril position giving different densities and textures. In the outer layer, the so-called primary wall (P) fibrils of about 10 nm in diameter are positioned crosswise to a layer of about 50 nm thickness. This crosswise positioning possibly impedes a swelling of the inner secondary wall. The secondary wall (S) consists of two layers S1 and S2. The thickness of the S1 layer is, in the case of cotton, about 100 nm, in the case of a spruce pulp fiber, about 300 nm. The fibrils are aligned parallel and densely packed in a flat helix, the direction of which may be opposite in subsequent S1 layers. The S1

layer can strongly impede swelling of the S2 layer beneath it, the thickness of which amounts to several μm and thus contains most of the cellulose mass. The fibrils are well aligned in a helix. In the cotton fiber, a layered structure of S2 exists due to density fluctuations during growth, with an average distance of 100–200 nm, which becomes visible after suitable swelling treatment. The inner layer closest to the fiber lumen, i.e. the tertiary layer (T) in the case of wood fibers and the S3 layer in the case of cotton, is comparably thin and has the fibrils aligned in a flat helix.

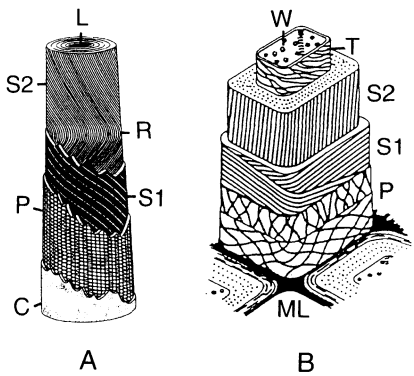

Figure 2.1.11. Scheme of the 'morphological architecture' of a cotton fiber (A) and a delignified spruce wood fiber (B) (Krässig, 1993); C–cuticle (rich in pectins and waxes), L–lumen, ML–middle lamella (mainly lignin), P–primary wall, R–reversal of the fibril spiral, S1–secondary wall ('winding layer'), S2–secondary wall (main body), T–tertiary wall, W–wart layer.

2.1.4 Pore structure and inner surface

Complementary to the fibril architecture of the fiber cell wall is a system of pores, capillaries, voids, and interstices. These pores are by no means uniform in size and shape, and besides a total pore volume and an average pore size parameter, information on size distribution and even on the shape of the pores would be necessary for a complete description of the pore system, which plays a decisive role in all heterogeneous chemical reactions of cellulose.

Quantitative information on pore volume and pore size is available by small-angle X-ray scattering (SAXS) in the range of 2–80 nm and by mercury porosimetry in the range of about 15–1000 nm of pore diameter. The latter technique, however, is limited to voids available from the fiber surface (Paul and Bartsch, 1972). SAXS and mercury porosimetry overlap somewhat with regard to pore size range covered and supplement each other with respect to pore criterion assessed. A detailed discussion of SAXS data with regard to pore structure

and inner surface of cellulose I and II is presented by Lin et al. (1987), where a "fractal structure of microcrystallite aggregates" is suggested for cotton cellulose. Information on the pore system is also available by size-exclusion chromatography, sorption measurements, and a calculation from fiber density. Tables 2.1.8 and 2.1.9 summarize some data obtained by SAXS and by mercury porosimetry with various cellulose samples.

Table 2.1.8. Data on pores of various cellulose samples as calculated by SAXS measurements (Fink and Walenta, 1994; Fink et al., 1992)

Sample	Volume of pores (%)	Inner surface of pores (m^2/g)	Parameter of average pore size (nm)
Cotton linters	1.7–1.8	5.3–6.0	11.6–13.1
Sulfite dissolving pulp	0.7–1.5	1.7–3.2	10.1–25.4
Sulfate pulp[a]	1.2	3.7	13.1
Cellulose powder[b]	1.4	5.2	10.4
Cellulose powder mercerized	1.7	15.8	4.4
Cellulose powder enzyme-treated	2.5	6.2	15.9

[a] Prehydrolyzed.
[b] Prepared from spruce sulfite pulp by partial hydrolysis and mechanical disintegration.

The data indicate a broad variability of pore criteria within the group of sulfate dissolving pulp. Mercerization of a level-off degree of polymerization (LODP) cellulose powder results in a significant decrease in pore diameter in connection with a remarkable enhancement of micropore surface. Enzyme treatment, on the other hand, obviously enlarges the existing pores, as to be concluded from the increase in pore volume and pore diameter (Fink et al., 1992).

As to be expected, the total pore volume assessed by mercury porosimetry considerably exceeds that obtained by SAXS due to inclusion of larger pores. Worth mentioning is the different pore structure of spruce and beech pulp, indicating a denser structure in the case of beech pulp.

Total pore volume and pore size distribution are very sensitive to swelling and drying treatments of the cellulose fiber samples: it has long been known that the first drying of cellulose results in a significant and irreversible reduction of the pore volume due to a so-called hornification by a tight cohesion of fibrillar ele-

ments. Interfibrillar and intercrystalline swelling in liquids like water or ethanol amine, however, leads to an increase in pore volume, which can be preserved by suitable drying techniques like freeze drying or solvent exchange.

Table 2.1.9. Voids in cellulose by mercury porosimetry (Quinn, 1963; Paul and Bartsch, 1972; Gröbe, 1989; Buschle-Diller et al., 1995)

Sample	Covered Pore size (nm)	Pore volume (cm^3/g)	Porosity[a] (%)
Cotton	>800	0.087	–
	>150	0.045	6.6
Spruce sulfite pulp	8000–400000	0.072	17.3
Viscose rayon	1100–150	0.073	–
	>15	0.018	–
Viscose staple fiber	8000–400000	0.018	6.6

[a] The term 'porosity' denotes the total percentage of pores including the large ones (>1000 nm).

Due to the pore and void system, the total surface area of cellulose fibers exceeds by far the geometrical outer surface. The so-called inner surface area is a decisive factor with regard to accessibility and reactivity in dissolution and derivatization processes of the polymer. The data published on inner surface area cover a wide range, from below 1 to about 1000 m^2/g, depending on origin and history of the sample, as well as on the procedure of determination. Data on the inner surface of cellulose are obtained by three routes:

(i) direct measurement of the interface by SAXS;

(ii) model calculation from a pore volume (determined by mercury porosimetry), assuming a defined shape of the pores;

(iii) sorption data of gases and vapors onto cellulose, usually evaluated according to the mehod of Brunauer, Emmett and Teller (BET). Sorbates frequently used are N_2, Ar, and water vapor.

Also the size-exclusion technique of Stone and Scallan (1967) has been used (cf. chapter 3).

Some data on the inner surface of cellulose materials obtained by N_2 sorption and supplied by Jacobasch (1984) are presented in Table 2.1.10.

Table 2.1.10. Inner surface of some cellulose samples calculated from N_2 sorption (Jacobasch, 1984)

Sample	Pretreatment	Surface (m^2/g)
Spruce sulfite pulp	–	0.35
Spruce sulfite pulp	H_2O swollen, freeze-dried	5.3
Cotton	–	0.60–0.72
Viscose rayon staple	–	0.3–0.4

The data indicate a much higher inner surface in the presence of water than that calculated from inert gas sorption in the dry nonswollen state.

Also organic dye molecules of defined shape, for example Kongo Red, have been employed for assessing an 'inner surface area' by adsorption experiments. A critical discussion of the latter technique is given by Heinemann (1985).

As already emphasized in connection with pore volume and pore size, the data on inner surface are strictly comparable only if assessed by the same technique, as the various procedures can differ on the one hand with regard to the size of accessible interstices, and on the other hand with regard to changes of the inner surface proper by interaction, e.g. swelling, of the cellulose with the substance employed.

Table 2.1.11. Inner surface of cellulose fibers determined by water vapor sorption

Sample	Inner surface (m^2/g)	References
Spruce pulp[a]	1000[b]	Stone and Scallan, 1967
Cotton	135	Krässig, 1993
Cotton flake	152	Brederick, 1989
Viscose cord rayon	292	Brederick, 1989
Viscose staple	292	Brederick, 1989
Microcrystalline cotton cellulose	135	Stone and Scallan, 1967
Microcrystalline cotton cellulose, mercerized	171	Stone and Scallan, 1967
'Amorphous' cellulose	434	Stone and Scallan, 1967

[a] Never dried.
[b] Size-exclusion.

Nevertheless, some conclusions of a more general nature can be drawn from the available data: the first drying of a cellulose fiber from the never-dried state

usually leads to a significant decrease in available inner surface area, which can only partially be reversed by subsequent reswelling. For cotton and cotton linters generally a smaller inner surface area has been reported compared to wood pulp. Under comparable conditions, viscose rayon and rayon staple exhibited a considerably higher inner surface than cotton (Brederick, 1989). For illustration of these rather general statements some data are compiled in Table 2.1.11.

Krässig (1993) obtained by water vapor sorption, an inner surface area of 135 m^2/g for a scoured and bleached cotton, which would correspond to an accessibility for aqueous media at the level of microfibrils of about 20 nm diameter.

2.1.5 The accessibility of cellulose

Chemical processing of cellulose proceeds during its whole course or at least in the initial phase in a heterogeneous reaction medium. Rate and final degree of conversion in these heterogeneous reactions depend strongly on the availability of the hydroxy groups in the anhydroglucose units, so-called accessibility (see also chapter 2.4). From the sight of cellulose structure, accessibility depends largely on the available inner surface, and also on supramolecular order and fibrillar architecture. But it is important to emphasize that the accessibility of a cellulose sample is by no means a constant structural parameter, as it depends decisively on the interaction considered. So for example only the AGUs situated at the inner surface of the pore and void system are accessible for sorption of inert gases, whereas even the cellulose chains in the highly ordered crystalline regions are accessible to aqueous NaOH of suitable concentration.

Due to this key-lock-principle of accessibility and type of interaction in question, the results obtained with the different methods of accessibility determination published (cf. Table 2.1.12) cannot be expected to coincide, and only data assessed by the same technique with different samples should be compared.

Accessibility data obtained from sorption experiments with inert gases like nitrogen or argon correspond closely to the inner surface area of the dry sample.

For a routine characterization of cellulose accessibility, often the interaction with water is employed, which is able to destroy weaker hydrogen bonds but cannot penetrate into the regions of high order. The amount of water vapor sorbed at definite temperature and relative humidity ('water regain') is one of the important criteria for describing the textile properties of native and regenerated cellulose fibers (Table 2.1.13).

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Table 2.1.12. Overview of methods for accessibility determination

Sorption of gases and vapors
– Sorption of N_2, Ar, or Kr
– Water vapor sorption ('water regain')
Interaction with liquid systems without chemical reaction
– Dimensional change or weight gain by swelling in water or organic liquids
– Size-exclusion techniques by measuring the take-up of molecules of defined size from aqueous solution (cf. chapter 3)
Exchange of H to D atoms at hydroxy groups of the AGU by interaction with D_2O
Partial chemical degradation or conversion by
– Ethanolysis of glycosidic bonds
– Xanthation in dispersion
– Esterification with formic acid or trifluoroacetic acid.
– Oxidation with N_2O_4 in CCl_4

Table 2.1.13. Water vapor regain and sorption ratio of cellulose fibers (58 % relative humidity, 21 °C) (Howsmon, 1949)

Sample	Water vapor regain (%)	Sorption ratio
Cotton linters	6.70	1.00
Wood pulp, untreated	8.05	1.20
Wood pulp, mercerized	10.45	1.56
Viscose rayon, standard	12.00–12.70	1.79–1.90
Viscose rayon, high tenacity	12.70–13.70	1.90–2.05

The so-called water retention value obtained by measuring the amount of liquid water retained by the swollen fiber moiety under defined conditions (Jayme and Rothamel, 1948) can still be considered as a valuable accessibility criterion for wood pulp and textile cellulose fibers despite the fact that its structural meaning is not very well defined. The exchange of hydrogen atoms of the cellulosic hydroxy groups by deuterium atoms via an interaction of the sample with liquid heavy water can be exactly investigated by determining the bound deuterium by infrared spectroscopy or more recently by high-resolution solid state NMR spectroscopy. This technique was therefore used rather frequently in the last decades to define and to determine an accessible part of the cellulose struc-

ture which was often considered to be identical with the so-called amorphous part of the structure.

A comparison of the D_2O-exchange (Frilette et al., 1948) accessible part and the X-ray amorphous part of various cellulose samples indicated a somewhat larger value for the former (Ioelovitch and Gordeev, 1994). These results were interpreted by a modified fringe fibril model, assuming a paracrystalline layer at the surfaces of the crystallites, which is accessible to D_2O, but is included in the crystalline part of the WAXS pattern.

Chemical procedures for determining an accessibility via the extent of a heterogeneous reaction like ethanolysis of glycosidic bonds, oxidation of AGU by N_2O_4, or esterification of accessible hydroxy groups with formic acid, have been employed to assess the effect of various production parameters on the supramolecular structure of man-made cellulose fibers. As demonstrated by the examples in Table 2.1.14, these chemical techniques sometimes permit a finer differentiation between samples than e.g. the water vapor sorption at 65 % relative humidity (r.h.).

Table 2.1.14. Effect of spin-stretch of viscose and rayon on accessibility, determined by ethanolysis and water vapor uptake (Philipp et al., 1967)

Spin-stretch (%)	Weight loss after ethanolysis and washing with H_2O (%)	Water vapor regain at 65% r.h., 120 °C (%)
20	41.8	14.6
40	35.5	14.3
60	28.5	14.0
80	24.0	13.8
100	23.4	13.8

A decrease in accessibility with increasing spin-stretch is indicated by both the procedures employed, but it is much more distinct from the weight loss on ethanolysis than from water vapor regain.

Furthermore, the data obtained by a stepwise intensification of the reaction via the reagent concentration or the reaction temperature can be evaluated to an accessibility spectrum of the sample in question, yielding more detailed information on its structural regions of low and medium order (Baudisch, 1965; chapter 2.4).

2.1.6 Alien substances associated with the cellulose matrix

A survey on molecular und supramolecular structure of cellulose cannot overlook the fact that cellulose is by no means delivered in a chemically pure form by nature, but requires steps of isolation and purification before chemical processing. Even after these refining steps small amounts of foreign compounds are still associated with the polymer. These alien substances, i.e. noncellulosic polysaccharides, fatty and waxy substances, as well as inorganic components, can caused problems in dissolution and derivatization of cellulose, and especially in transforming the polymer to artificial fibers via the state of solution.

Raw cotton linters contain only 80–90 % of cellulose. Purification is accomplished by a combination of mechanical sorting steps in order to remove gross impurities like seed shells with a mild alkali treatment at elevated temperature ('scouring'), eliminating proteins, fats, waxes, pectins, and other polysaccharides, usually followed by a bleaching process. By this method the content of, e.g., pentosans is reduced from the 1.5–2.0 % level to a level of 0.1–0.5 %.

Soft woods and hard woods, containing about one-third each of lignin, cellulose and hemicelluloses (mainly xylans, mannans, arabinans, and polyuronic acids), as well as some so-called accessory compounds, require a more drastic treatment in pulping and bleaching in order to arrive at a high-quality dissolving pulp, and these steps of isolation and purification are always accompanied by a significant decrease in *DP*. But even these dissolving pulps still contain some alien polysaccharides, which may influence the course of, e.g., a xanthation. A small amount of organo-soluble extractives can exert an undesired surfactant effect, and some inorganic matter can promote a clogging of spinnerets in artificial fiber spinning.

Especially the cations of Ca and Fe, as well as SiO_2, are considered to be detrimental in this respect. As quality criteria for dissolving pulps, usually the content of alkali-insoluble matter (R 10, R 18, see Table 2.1.15), corresponding fairly well with the content of long chain cellulose, the content of organo-soluble extractives, the amount and composition of ash, and sometimes the pentosan and the carboxyl content are used. The level required for these criteria depends on the subsequent chemical process. An especially high standard is, e.g., necessary for cellulose acetate manufacture, which is met either by the use of linters or by a special refining of wood pulp. Table 2.1.15 presents an overview on quality requirements for dissolving pulps employed in different conversion processes.

Table 2.1.15. Quality criteria for dissolving pulps (data provided by Zellcheming e.V., Darmstadt)

Quality parameter	Level required for				
	Cord rayon	Textile rayon	Standard rayon staple	CMC	Cellulose acetate
Brightness[a]	> 90	> 90	> 90	>89	> 90
R 18[a]	> 99	> 92	> 90	>90	> 96
R 10[a]	> 98	> 90	> 87	>87	> 94
Pentosane content[a]	< 2	< 4.5	< 4.5	-	< 1
DCM-Extract[a]	< 0.02	< 0.2	< 0.2	< 0.3	< 0.12
Ash[a]	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
SiO_2[a]	< 50	<250	<250	-	< 50
Ca[b]	<250	< 10	< 10	-	< 100
Fe[b]	< 10	< 10	< 10	-	< 5
Mn[b]	< 1	< 1	< 1	-	< 1

[a] - in %.
[b] - in mg/kg
CMC - Carboxymethylcellulose
R 18 Insoluble residue in 18% aqueous NaOH
R 10 Insoluble residue in 10% aqueous NaOH
DCM-Extraxt Dichloromethane extraxt

2.1.7 Macroscopic properties of cellulose

2.1.7.1 General properties and gross morphology

Cellulose is a colorless, odorless, and nontoxic polymer solid. It is insoluble in water and common organic solvents, but swellable in many polar protic and aprotic liquids (see chapter 2.2). Due to the strong cohesion between the macromolecules via intermolecular forces, especially a hydrogen-bond network, cellulose cannot be transformed into the molten state.

Due to its molecular structure, supramolecular order and fibrillar morphology, cellulose is a typical fiber polymer and is quite predominantly processed and used in the form of fibers. The polymer is available from nature in the form of various plant fibers and as wood pulp after delignification of woody plants. Table 2.1.16 gives a survey on the fiber dimensions of various natural fibers and wood pulps.

As a starting material for chemical transformation of cellulose, rather exclusively dissolving-grade wood pulps and to some extent bleached and scoured

Table 2.1.16. Average fiber dimensions of some cellulose raw materials (data supplied by E.W. Unger, Technical University of Dresden)

Cellulose material	Fiber length (μm)	Fiber width (μm)
Spruce	3400	31
Pine	3100	25
Beech	1200	21
Eucalypt	850	20
Bamboo	2700	14
Wheat straw	1410	15
Bagasse	1700	20
Cotton linters	9000	19

cotton linters are used. Man-made cellulose threads usually manufactured by the viscose process are supplied as rayon staple or rayon endless filament.

The fiber dimensions of cellulosics can be cut down by various milling procedures. Wet milling, for example in a paper-makers beater, predominantly exerts a fibrillating action, but can also considerably decrease the average fiber length in dependence on the technique applied. Dry milling in an impact or attrition mill loosens the fiber structure and results in a considerable decrease in fiber length. Cutting down the average fiber length can be essential in chemical processing of rather long-fiber cellulosic materials like cotton linters. A too high fiber length can lead to a so-called spinning of fibers around the stirring equipment in the reaction vessel. Prolonged ball milling of dry cellulose fibers leads to rather complete destruction of fibrillar morphology and supramolecular order, and finally results in an amorphous cellulose of rather low *DP*. Commercial cellulose powders mainly used as sorbents are manufactured either by dry milling alone or by a combination of acid hydrolysis and mechanical disintegration. The morphology of these products and as a consequence their colloidal properties can be varied within rather wide limits via the special procedure employed (Philipp et al., 1982). Wood pulp is usually supplied as dry sheets or rolls with a water content of about 10 %, or in the wet state with about 50 % water content.

The end-use gross morphology of cellulosics is generally that of a two-dimensional sheet structure, obtained either by textile processing in the form of fabrics with well-defined separated single threads, or in the form of paper sheets with the single pulp fibers strongly cohering via interfiber hydrogen bonds and by gluing with the components of paper-makers glue. At the other extreme, a gross morphology in the form of a transparent film of regenerated cellulose is obtained by casting from a cellulose solution, exhibiting no indication of a fiber or fibrillar macrostructure. By changing and adjusting the conditions of pulp

beating, paper sheet formation, and subsequent pressing and drying during paper making, a rather continuous change of gross structure from a coarse network of individual fibers to a nearly structureless film-like sheet can be achieved.

2.1.7.2 Mechanical properties of cellulose

Due to its linear polymer chains, the strong cohesion between the macromolecule and the high supramolecular order, as well as its fibrillar morphology, cellulose is a rather ideal fibrous polymer. Thus considerations on mechanical properties of cellulose are usually centered on criteria relevant to textile end-use, for example breaking strength (tenacity) or elongation at break. This 'textile mechanics' of cellulose today constitutes an area of science of its own, just like the mechanics of paper sheets, which, however, is of minor relevance in connection with the organic chemistry of cellulose and therefore will only be mentioned briefly here.

Due to imperfections of structure at the different levels, the measured breaking strength is much lower than the theoretically calculated ultimate tensile strength, and varies within wide limits depending on fiber structure (Table 2.1.17). The same large variability is observed in the shape of the stress–strain curves of different cellulosic fibers as demonstrated in Fig. 2.1.12 where the stress is given in gram per fiber fineness messured in grex.

Table 2.1.17. Mechanical data of cellulose filaments and fibers of various origin (Meredith, 1946)

Specimen	Initial Young's modulus (g/grex)	Breaking elongation (%)	Breaking strength (g/grex)	Work of rupture (toughness) (g cm/grex)
Cotton	50	7.3	3.1	0.10
Flax	183	3.0	5.5	0.08
Hemp	183	2.6	4.7	0.06
Jute	176	1.8	3.6	0.03
Ramie	149	3.7	6.0	0.11
Textile viscose	58	21	1.9	0.23
Stretched viscose	153	5.8	5.0	0.15
Acetate rayon	28	29	1.2	0.22
Silk	77	26	4.4	0.74
Nylon	27	26	4.8	0.77
Wool	25	38	1.3	0.32

grex = international unit of fiber fineness

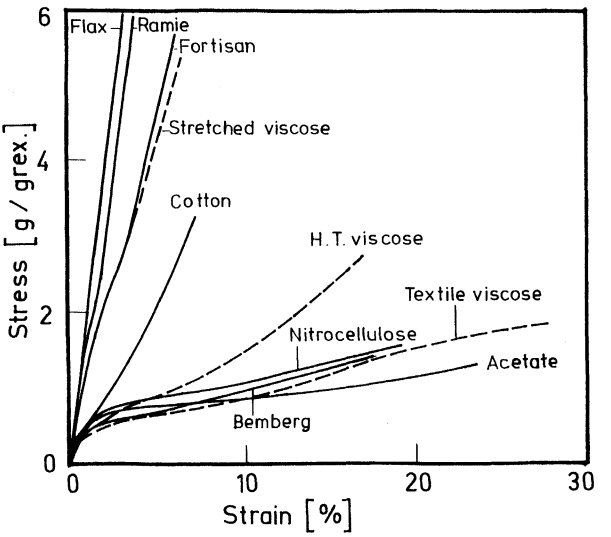

Figure 2.1.12. Stress–strain curves of cellulose threads (Meredith, 1946); H.T. means high tenacity

Oven-dried cellulose, which exhibits a strong hygroscopicity, is comparably brittle. Water exerts a strong softening action on cellulose fibers by interacting with the hydrogen-bond system, and this softening action is reflected by a flatter stress–strain curve. In the wet state, after immersion in water, the tenacity can decrease or increase due to the two counteracting effects of this softening action on one hand and a more uniform stress distribution on the other. The second effect is responsible for the higher tenacity of wet cotton fibers in comparison with the dry sample, while the softening action terminates with regenerated cellulose fibers coursing a considerable reduction in tenacity on going from the dry to the wet state.

Air-dried cellulose is rather resistant to mechanical impact and a large amount of mechanical energy has to be spent in order to destroy the macroscopic and microscopic structure. A prolonged oven-drying, or freezing of the sample can reduce the toughness and facilitate mechanical disintegration.

A special comment seems to be necessary regarding the very complex flow properties of cellulose suspensions which are essential not only in the course of paper manufacture, but also during chemical processing of cellulose. The principles of rheology of these systems rely mainly on the swelling power of the liquid medium, on the size and shape of the polymer particles, and on the cellulose concentration. In a nonswelling organic liquid a quick separation of the polymer phase occurs after discontinuing mechanical agitation, and the suspension viscosity on stirring remains rather low. In water and other liquids of high swelling

power (cf. chapter 2.2), a more or less stable suspension remains after stirring, especially in the case of powder cellulose, and the flow properties are very complex, showing for example 'slip stick' effects at the wall confining the system. Transformation of a two-phase system consisting of cellulose fibers and a swelling liquid into a homogeneous one-phase system during dissolution with or without chemical reaction requires a large amount of mechanical energy in passing a gel-like transition state. With the normal equipment of an organic chemistry lab, only systems with a few percent of cellulose can be handled; at higher cellulose concentrations, up to about 10 %, special kneading and stirring equipment permitting a high energy input has to be employed.

2.1.7.3 Electrical, optical, and thermal properties of cellulose

Bone dry cellulose is a good insulator with a specific direct current (dc) resistivity of about 10^{18} Ω cm and has been amply used in the fiber or sheet form for this purpose, for example as insulating paper in electrical condensors. But the dc resistivity decreases significantly with increasing water content and increasing content of ions or ionic sites (Table 2.1.18).

Table 2.1.18. Specific resistance of cellulose (Gröbe, 1989)

Cellulose sample	Relative humidity (%)	Specific resistance (Ωcm)
Pure dry cellulose		1×10^{18}
Cotton (30 °C, single film)	52%	2×10^{7}
	62%	1×10^{7}
	75%	7×10^{5}
	85%	3×10^{5}
Viscose rayon	75%	3×10^{6}
	85%	1×10^{2}

Table 2.1.19. Dielectric constants of cellulose (Gröbe, 1989)

Specimen	Rel. humidity (%)	Dielectric constant at:	
		1 kHz	100 kHz
Cotton	0	3.2	3.0
	45	7.1	4.4
	65	10.0	6.0
Viscose rayon	0	3.6	3.5
	45	5.4	4.7
	65	8.4	5.3

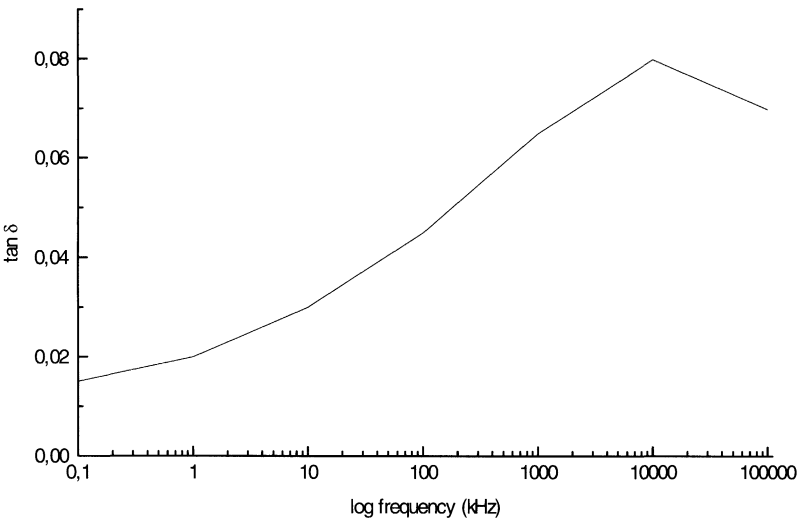

Figure 2.1.13. Dielectric loss curve of cellulose at 20 °C (based on data from Gröbe, 1989).

Dielectric constants of cellulose in dependence on relative humidity are presented in Table 2.1.19, and Fig. 2.1.13 depicts a dielectric loss curve in dependence on frequency.

Concerning optical appearance, cellulose fibers and fiber assemblies are white and nontransparent due to their pore and void system, but transparent films can be obtained by casting from solution, and opaque specimens are available by high-pressure treatment of cellulose powder.

Due to a preferential orientation of the macromolecules along the fiber axis, cellulose I as well as cellulose II exhibits birefringence (see Table 2.1.20), which, however, lags behind the theoretical value in the case of regenerated cellulose fibers due to incomplete chain orientation.

Table 2.1.20. Refractive indices and birefringence of cellulose (Gröbe, 1989)

Sample	$n \parallel^a$	$n \perp^b$	$n \parallel - n \perp$
Ideally oriented cellulose I	1.618	1.544	0.047
Cotton	1.576–1.595	1.527–1.534	0.045–0.062
Ideally oriented cellulose II	1.578	1.523	0.055; 0.054
Viscose rayon staple	1.529–1.547	1.512–1.520	0.013–0.034

[a] parallel
[b] perpendicular

Table 2.1.21. Thermal data on cellulose (according to Gröbe, 1989)

Glass transition temperature	230 °C
	230—245 °C
Specific heat cotton	0.291 cal/g degree
rayon	0.317
Thermal conductivity rayon staple	ca. 5 x 10^{-4} cal/g cm degree
	0.071 W/m degree
Coefficient of thermal expansion	
cotton linters	(-30—25°C): 4 x 10^{-4} degree^{-1}
Heat of crystallization, extra purified, 100% crystallinity	25.3 ± 1.2 cal/g
Heat of transition Cell I → Cell II	38.1 kJ/kg
Heat of thermal transition at 120—140 °C	109—147 J/g

Important for structure elucidation and for chemical derivatization is the infrared spectrum of cellulose. IR bands of cellulose and their assignment are listed in chapter 3 of this book.

Of some practical relevance to cellulosics is the remittance curve, i.e. the spectral curve of remitted light, as a high brightness without a yellowish hue is usually desired. For cellulose in sheet form (pulp sheet, paper sheet) this brightness is often determined (Tappi Standard T 452, OM 92) by comparison with a TiO_2 powder standard at a wavelength of 457 nm and a beam entrance angle of 45°. For dissolving pulps, a brightness of ≥ 90 % is generally expected today.

Some thermal properties of cellulose, taken from Gröbe (1989), are summarized in Table 2.1.21.

Cellulose can be considered as a thermally rather stable polymer, as it retains its solid state structure and its mechanical properties up to a temperature of about 200 °C. Above this temperature the thermal decomposition starts (cf. chapter 2.3), and a melting point assumed to be about 400 °C, cannot be realized experimentally. In accordance with the nature of cellulose as a semicrystalline polymer, several more-or-less well-defined thermal transition regions have been reported in the literature (see Table 2.1.21).

2.1.7.4 Chemical stability and environmental properties of cellulose

Like many other organic polymers, cellulose is rather an inert polymer and can be combined with other classes of construction materials. Blends of wood com-

patible with other polar polymers like polyacrylonitrile, polyurethanes, or polyamides have been reported in recent years.

Cellulose remains stable in water of neutral or slightly alkaline pH, as well as in a large number of organic liquids of different polarity, but is swollen in these media to a varying extent (cf. chapter 2.2). On the other hand, the polymer is susceptible to several routes of degradation, the mechanism of which will be discussed in chapter 2.3. Of high practical relevance are:

(i) the hydrolytic degradation in acid aqueous, as well as nonaqueous, media by cleavage of the glucosidic bond;

(ii) the hydrolytic cleavage of the glucosidic bond in water or in a moist environment catalyzed by cellulolytic enzymes of various fungi and bacteria as the basic process in rotting of cellulose;

(iii) oxidation processes proceeding via several pathways resulting in an introduction of carbonyl and carboxylic groups, and finally in chain cleavage to various fragments, a process to be avoided in cellulose bleaching with chlorine-containing bleach, as well as with chlorine-free oxidants;

(iv) a thermal degradation at a temperature above 180–200 °C along various and rather complex reaction routes, leading to gaseous products on the one hand, and char on the other; a process that can be controlled and deliberately influenced by various flame retardant additives to cellulose fibers.

A physicochemical peculiarity of cellulose is its strong sorption power and high sorption capacity for many classes of substances. The sorption of water vapor already mentioned is one of the practically most relevant examples. At low relative humidity a strong chemisorption of H_2O molecules by interaction with the hydroxy groups of the polymer takes place, followed by a multilayer sorption at medium relative humidity, and a capillary condensation of free water at high relative humidity.

Further details on water vapor sorption, as well as on swelling of cellulose in liquid water or in various organic liquids will be considered in detail in chapter 2.2. It must be emphasized already here that many classes of organic compounds, especially various classes of dyes and also inorganic cations, especially of higher valency like calcium or iron(III), are easily and quickly sorbed onto cellulose fibers, the latter obviously not only at the carboxylic sites but also by a chelation action of the cellulose hydroxylic groups (Jacopian et al., 1975). An example of practical interest is the elimination of small amounts of iron ions from aqueous alkali by sorption onto cotton. Also the sorptive binding of alien polysaccharides of lower molar mass, for example xylanes, is to be mentioned here.

Cellulose and many cellulose products are favorable polymers from the viewpoint of the environment, as they can be safely returned to the natural carbon cycle by simple rotting. As already mentioned cellulose is not toxic to living organisms, including humans, if introduced via the gastrointestinal tract. It is excreted without

chemical change by humans and other classes of mammals. As the postmigration of cellulose powder particles through the intestinal wall, which was rigorously discussed about 15 years ago, can be ruled out by recent experiments (Steege et al., 1978), this is not to be considered any longer as a hindrance to the application of cellulose powders to pharmaceuticals and food products.

Summarizing this subchapter, it should be stressed that the principle assets of cellulose as a polymer material are to be seen in its hydrophilicity, in combination with good mechanical properties, its potential as a sorbent, its nontoxicity, and last but not least, its safe disposability after use.

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2.2 Swelling and Dissolution of Cellulose

The dissolution or at least a considerable limited swelling of the cellulose moiety is an indispensable prerequisite for a subsequent controlled cellulose functionalization. Without at least some swelling, a reaction only at the available surface layer is possible, as demonstrated by special procedures of acetylation. After a limited swelling, the gross structure of the cellulose sample as a moiety of particles or fibers or as a film is largely maintained despite an increase in sample volume due to uptake of swelling agent and significant changes of the physical properties. On dissolution a transition from a two-phase system to a one-phase system takes place, and the original supramolecular structure of the sample is destroyed.

Despite these differences the phenomena of swelling and of dissolution have many common features, especially from the physicochemical point of view: in both cases the intermolecular forces between the macromolecules are overcome by an in summa stronger interaction leading to a loosening or even an elimination of cellulose supramolecular structure. Both the processes of swelling and of dissolution serve the purpose of enhancing the accessibility of the cellulosic hydroxy groups for a subsequent reaction. Furthermore, there is no clear cut borderline between a swelling and a dissolution process, and the same system can act either as a swelling agent or as a solvent depending on the *DP* and the structure of the cellulose sample. It is interesting to note that trimethylbenzylammonium hydroxide/water leads to a limited swelling of the polymer, while triethylbenzylammonium hydroxide/water dissolves cellulose (Strepicheev et al., 1957). This means minor changes in constitution may be responsible for whether a compound dissolves or only swells the polymer.

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With regard to cellulose functionalization, it should be mentioned here already that swelling and dissolution may occur simultaneously during the intended reaction in the reaction medium. But more often in the organic chemistry of cellulose, a two-step process is preferred, with the first step consisting of a so-called activation, i.e. loosening of cellulose physical structure by swelling, followed by the second step, i.e. the intended reaction proceeding either with the swollen sample in a heterogeneous manner, or together with dissolution. As artificial solid state cellulose structures, i.e. man-made films or fibers, are predominantly obtained industrially via the dissolved state of the polymer, a brief survey of some principles of cellulose solid state structure formation is included into this chapter.

2.2.1 Limited swelling of cellulose

Limited swelling in aqueous as well as in nonaqueous media can occur in the easily accessible regions of cellulose only, or can affect the crystalline regions too. In both cases intermolecular bonds between the polymer chains are broken to a variable extent but the intermolecular cohesion between the polymer chains is still maintained even in the case of the intracrystalline swelling, mainly due to the limited solvation of the interaction compound formed.

If swelling takes place in the easily accessible regions only (intercrystalline swelling), the increase in weight and volume of the sample results from a filling of the pore system by the swelling medium, combined with a rupture of interfibrillar bonds (Schleicher, 1983a) and from the uptake of swelling agent. In the case of intracrystalline swelling, usually an additional increase in lattice dimensions of the crystalline regions takes place, often resulting in an increase of one of the lattice spacings due to a so-called layer lattice reaction of the swelling agent with the cellulose moiety.

From a chemical point of view, limited swelling can be considered as a competition in hydrogen-bond formation between cellulosic hydroxy groups and suitable groups of the swelling agent in the case of the rather strong swelling encountered with polar protic systems. In the case of low swelling power with many organic liquids, the other intermolecular forces also have to be considered in contributing to the swelling effect.

It is of course not possible within the framework of this book to consider all the systems known today with regard to their swelling power for cellulose. Therefore only some typical examples relevant to organic chemistry of cellulose derivatization will be treated here in some detail:

(i) the swelling in some simple liquids often used as reaction media;
(ii) the swelling action of aqueous sodium hydroxide and related systems;
(iii) the limited swelling in two- or multi-component solvent systems below a critical concentration of the active component.

For a quantitative determination of swelling, usually the mass uptake of swelling agent related to sample weight is used. A procedure first described by Jayme and Rothamel (1948) for the determination of the so-called water retention value has been found to be generally applicable and rather convenient (see chapters 2.2.1.1 and 3). The precision of this method is generally within 5 % of the swelling value, with cellulose samples in the form of fibers, films, or rather coarse particles.

2.2.1.1 Swelling of cellulose in water

Interaction between cellulose and water plays an important part in the chemistry, physics, and technology of cellulose isolation and processing, and it is the fundamental process in papermaking. Cellulose exhibits a high hygroscopicity due to interaction of its hydroxy groups with water molecules, but is hindered from being dissolved in water by its ordered supramolecular structure. Cellulose–water interaction can be understood as a competition of hydrogen-bond formation between hydroxy groups of the polymer and hydrogen-bond formation between one hydroxy group of a cellulose chain and a water molecule or a water cluster (cf. Fig. 2.2.1).

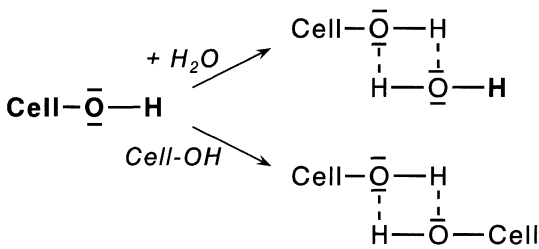


Figure 2.2.1. Schematic depiction of competition between hydrogen bonding of a cellulose hydroxy group with a water molecule and another cellulose hydroxy group.

Cellulose–water interaction thus depends strongly on the supramolecular structure of the specimen in question, on the amount of water already present in the polymer, and also on factors such as temperature, which influence water structure. At least with native cellulose, cellulose–water interaction is limited to the non-crystalline structural regions and the pore and void system. As cellulose–water interaction interferes with the inter- and intramolecular hydrogen bonds of the cellulose structure, it is usually not completely reversible after drying, and pronounced changes in cellulose physical structure can occur. A small amount of water is bound rather strongly to the free hydroxy groups of an excess of bone dry cellulose in a strongly exothermic reaction, with a heat of

reaction of 4.3 kcal/mol of water. This enthalpy change decreases strongly, however, with an increase in water content already bound (Götze, 1967).

Sorption of water from the vapor state has been considered already in the previous chapter in connection with cellulose accessibility (chapter 2.1). The sigmoidal shape of the sorption isotherm in dependence on relative humidity (see Fig. 2.2.2) results from a superposition of chemisorption of water molecules onto free hydroxy groups, a mono- and multilayer formation of water molecules at the accessible surfaces, and a capillary condensation in the pore and void system enlarged by the sorption and swelling process itself.

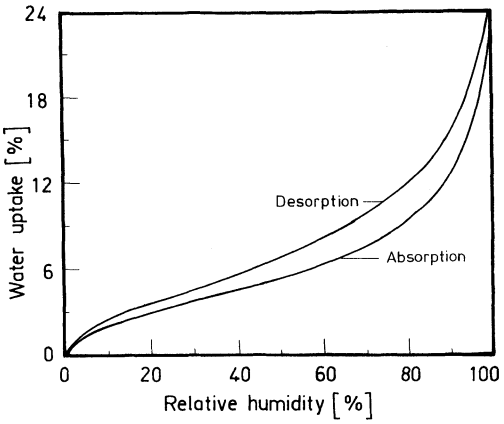


Figure 2.2.2. Hysteresis of water vapor sorption and desorption of scoured cotton, (Urquhardt and Williams, 1924).

This superposition is reflected by the curves in Fig. 2.2.3 for the amount of so-called bound water and so-called free water in relation to relative humidity.

At a given relative humidity the total water vapor uptake depends largely on cellulose physical structure, and is significantly higher for rayon than for cotton, as already discussed in connection with moisture regain (see chapter 2.1).

As illustrated by Fig. 2.2.2 for a scoured cotton sample, sorption and desorption isotherms do not coincide, but show a hysteresis with the desorption lagging behind.

This hysteresis can be traced back to positional changes of structural entities due to the previous sorption process and/or to a pertinacious binding of the last traces of water on full desorption. The first mentioned cause is in agreement with the observation that water vapor sorption is connected with a small increase in fiber volume at the level of 1 %.

The time dependency of water vapor sorption by a spruce sulfite pulp at different relative humidities is shown in Fig. 2.2.4. In agreement with the different mechanisms already discussed for water vapor uptake, a first-order rate law was

found adequate to evaluate the sorption curves at low relative humidity. Above 70–80 % relative humidity, however, water vapor sorption followed the rate law of swelling, i.e. $dQ/dt = k\ (Q_\infty - Q_t)^2$, where Q_∞ is the equilibrium value of water uptake.

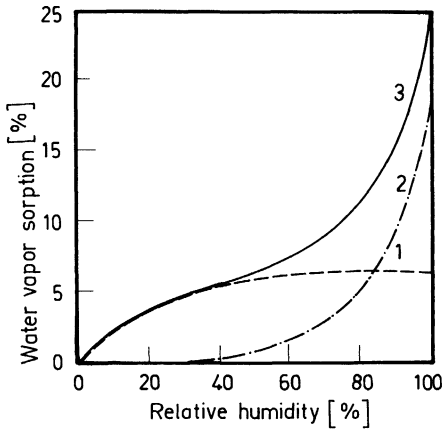


Figure 2.2.3. Total water vapor sorption of cellulose as the sum of 'bound' water and 'free' water: (1) bound water; (2) free water; (3) total water sorbed (Meredith and Preston, 1932).

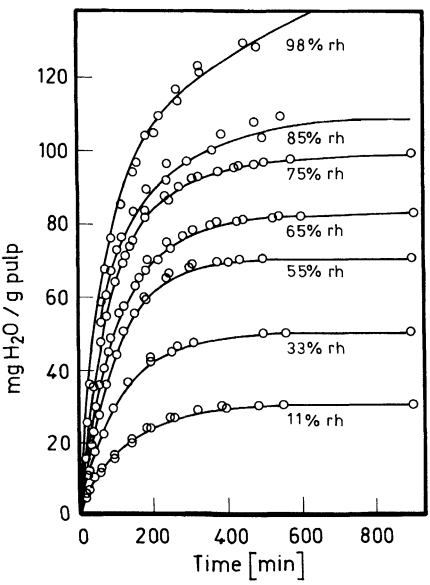


Figure 2.2.4. Course of water vapor sorption at various relative humidities (r.h.) of spruce sulfite pulp, predried at 20 °C (Philipp, 1952).

At the so-called fiber saturation point, i.e. at a relative humidity of 100 %, water vapor uptake coincides widely with the amount of water imbibed by swelling in liquid water.

The uptake of liquid water to be discussed now is usually assessed by the weight gain of the dry sample or by its change in fiber dimensions. A criterion often employed is the so-called water retention value (WRV) (Jayme and Rothamel, 1948), i.e. the weight gain (%) of a dry sample after swelling in a large excess of water and subsequent centrifugation under defined conditions (for further details see chapter 3).

The equilibrium WRVs listed in Table 2.2.1 demonstrate the decisive influence of cellulose supramolecular structure on water swelling. This effect is reflected also by the data in Table 2.2.2. With all the samples listed here the major part of the imbibed water is present as the so-called free water in capillaries, pores, and voids of the structure, while a minor part is more or less tidily bound by chemisorption to accessible surfaces. This bound water shows deviations from the properties of bulk water as it is considered as nonfreezing and not participating in dissolution of inorganic salts.

According to Stamm (1956), up to seven layers of water molecules sorbed on a cellulose surface can belong to the bound part of swelling water. In the case of regenerated cellulose, some WAXS evidence is available indicating that a small amount of water can penetrate also into the crystalline parts of the structure (Koblitz and Kiessig, 1960, see Table 2.2.2), as concluded, for example, from the increase of the 1-0-1 lattice distance (A_0) from 0.73 to 0.77 nm.

The existence of defined cellulose hydrates after water swelling of regenerated cellulose is still a matter of discussion and shall not be considered further here. A characteristic cellulose hydrate was obtained by decomposition of cellulosic compounds, e.g. alkali cellulose, at low temperature ('water cellulose') (Sakurada and Hutino, 1936).

Table 2.2.1. Water retention values (WRV) of some native and regenerated cellulose samples (Koblitz an Kiessig, 1960)

Sample	WRV (%)
Cotton	51
Spruce sulfite pulp	63
Spruce sulfite pulp, hydrolyzed to LODP	60
Spruce sulfite pulp, decrystallized by amine	87
Spruce sulfite pulp, mercerized	82
Pine sulfate pulp, never dried	135
Pine sulfate pulp, air dried	84
Rayon staple, never dried	95
Rayon staple, air dried	86
Cuprammonium rayon, air dried	96

Table 2.2.2. Equilibrium uptake of liquid water by native and regenerated cellulose (Koblitz and Kiessig, 1960)

Sample	Equilibrium uptake of water (% of sample weight)			
	Total H_2O	Free H_2O	Bound H_2O	Crystal H_2O
Cotton	49.9	35.0	14.9	0.0
Linters pulp	39.4	47.5	11.9	0.0
Supercord rayon	64.1	30.4	25.7	3.7
Cord rayon, standard grade	90.2	60.2	30.0	3.7
Textile rayon, standard grade	118.5	92.7	25.8	3.7

As shown by the data in Table 2.2.3, the increase in fiber volume on swelling in water is predominantly caused by a lateral swelling, i.e. an increase in fiber cross sections or fiber width, whereas the length of the fiber is changed to a small extent only.

Table 2.2.3. Change in fiber dimensions of various cellulose fibers due to swelling (equilibrium state) in water (data as compiled by Götze, 1967)

Sample	Cross section (%)	Length (%)	Width (%)	References
Cotton	48.6	+ 0.1	14	Collins, 1931
Cotton linters	21	–	–	Morehead, 1952
Cord rayon	50	–	–	Morehead, 1952
Textile rayon	65	–	–	Morehead, 1952
Rayon	65	3–5	26	Preston and Das Gupta, 1947

This anisotropy of swelling obviously results from a more or less perfect orientation of the cellulose fibrils along the fiber axis with ideal orientation, leading to transversal swelling only.

Swelling of cellulose in liquid water can be widely reversed by drying, with the time of drying depending on the amount of water imbibed, and thus being much longer for rayon than for cotton. A cyclic swelling and drying results in a lowering of the swelling value of cotton as well as of rayon, obviously due to a better stepwise alignment of supramolecular entities. Water swelling of cellulose fibers proceeds very fast, i.e. within seconds. The rate of swelling in liquid water is determined by the time of wetting, i.e. by the hydrophilicity of the fiber sur-

face (Mann and Morton, 1954). This is in well agreement with the significant decrease in swelling rate observed after predrying a spruce sulfite pulp at 105 °C (Schwabe and Philipp, 1954).

The dependency of swelling rate on the predrying temperature of the same pulp is illustrated in Fig. 2.2.5, showing the amount of water soaked by a stripe of pulp under defined conditions after 5 and after 10 min.

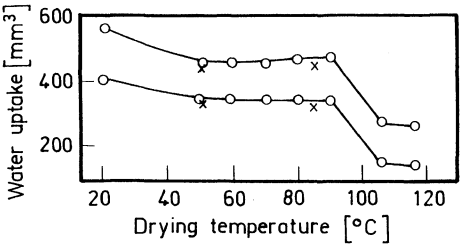


Figure 2.2.5. Water uptake by a spruce sulfite pulp stripe in dependence on pulp predrying, after 5 (bottom) and 10 min (top) soaking time (Schwabe and Philipp, 1954); O dried in air, X dried in vacuum.

After a flat decrease up to a predrying temperature of 90 °C, a steep drop in swelling rate is observed in the range between 90 and 110 °C due to surface hornification.

From the ample experimental evidence on water swelling of cellulose, abridged here only very briefly, can be concluded that the uptake of liquid water comprises a chemisorption of water molecules in the accessible regions of the structure, as well as an imbibition of liquid water into the pore and void structure, and that the usually very fast rate of swelling is governed by the hydrophobicity/hydrophilicity balance of the fiber surface at the moment of contact with the liquid. The increase in fiber volume due to the expansion of the fibrillar network by the so-called swelling pressure can be traced back (Bartunek, 1952 and 1953) predominantly to changes in the water structure on contact with the polymer, i.e. the decay of water clusters originally present on contact with cellulosic hydroxy groups resulting in a volume increase of the liquid.

Concerning the practical relevance of water swelling, its role in papermaking by formation and decomposition of cellulose–water hydrogen bonds has been already mentioned. Besides this, water uptake by swelling and its consequences on the material properties of cellulosic materials results in advantages as well as in limitations in their practical use. In connection with cellulose derivatization, the strong and fast water swelling of native as well as of regenerated cellulose is a valuable and frequently employed means of cellulose activation (see chapter 2.4) for subsequent chemical transformations in nonaqueous systems, as the high swelling value can be retained by an adequate solvent exchange with liquids of

decreasing polarities (see chapter 2.2.2). As another route to enhance solubility and reactivity of cellulose via interaction with water, the so-called steam explosion process shall be finally mentioned (Yamashiki et al., 1990): wood pulp, preferably spruce sulfite pulp, is brought into contact with steam at high pressure, which is then suddenly released. This results in a disruption of the fibrillar network and a loosening of physical structure, but also in a considerable thermohydrolytic chain degradation (see chapter 2.3). This route of 'activation on the morphological level' was probably intended especially for making wood cellulose soluble in aqueous alkali, but to the authors' knowledge a large-scale realization has not yet been reported.

Besides cellulose–water interaction itself, the depletion of cellulose from sorbed and imbibed water by drying plays an important part in many areas of cellulose processing. The completeness of drying can be essential in subsequent derivatization reactions under aprotic conditions. The course of drying determines the changes in fibrillar structure and pore system, and eventually results in a significant decrease in accessibility due to surface hornification. As revealed by ^{1}H-NMR imaging, even a very slow drying of a cellulose fiber moiety, e.g. a pulp sheet, results in a gradient of water content across this specimen. Obviously the water is evaporated faster from the surface than is delivered from the interior of the specimen by capillary transport (Nilsson et al., 1996).

In studies on cyclic drying and wetting of soft wood sulfate pulp the decisive effect of first drying on fibre dimensions, fibre wall thickness and pore volume was emphasized (Bawden and Kibblewhite, 1997).

2.2.1.2 Limited swelling of cellulose in some organic liquids in comparison with water

Swelling of cellulose in water and aqueous systems has been investigated thoroughly for many decades in connection with the use of cellulosic fibers in textiles and with papermaking. In contrast, data on swelling of cellulose in organic liquids are still rather scarce, but are of relevance of course in connection with cellulose functionalization in nonaqueous media.

As illustrated by the data presented in Table 2.2.4, the equilibrium swelling value depends on the liquid concerned as well as on the structure of the cellulose sample. Despite the strong influence of supramolecular structure, the ranking of different liquids as swelling agents for cellulose generally remains the same with samples differing strongly in structure. As can be seen from the data, water takes an intermediate position within the series of swelling media. Some protic as well as aprotic organic liquids show a significantly higher swelling power, e.g. formamide, dimethyl sulfoxide (DMSO), or ethanolamine.

Table 2.2.4. Effect of swelling medium and polymer structure on the swelling of cellulose in organic liquids at 20 °C (Wagenknecht, 1976)

Swelling medium	Equilibrium LRV (%)					
	Cotton	Hydrol. linters	Spruce untreated	sulfite pulp decryst.	mercerized	Rayon staple
Ethanolamine	106	71	163	189	192	256
DMSO	90	72	121	168	170	186
Formamide	71	58	88	158	106	105
Water	51	45	63	87	82	86
DMF	49	25	63	113	–	69[a]
Acetic acid	36	13	45	92	33	30
Ethanol	21	14	32	22	29	20
n-Hexane	12	7	15	–	14	13

[a]After 2 months.
DMF, *N*,*N*-dimethylformamide; LRV, liquid retention value.

On the other hand, most of the well-known organic liquids like alcohols give rise to a much smaller swelling only.

According to Schleicher 1983a and Wagenknecht 1976, no general correlation between one single parameter of the liquid and the swelling value of cellulose can be found. In general a high hydrogen-bond-forming activity of the liquid and/or a high polarity is connected with a rather high swelling power. An increase in molar volume may impede swelling due to a diminished penetration of the liquid into the cellulose structure, especially in the case of regenerated cellulose (cellulose II), as shown by some examples in Table 2.2.5.

According to Schleicher (1983b), a statistical correlation exists between the swelling value (LRV) and the sum of the squared donor number and the squared acceptor number of the liquid concerned. Liquids capable of forming nitrogen hydrogen-bonds, often show a stronger swelling power than comparable ones forming oxygen hydrogen-bonds, as demonstrated by some examples in Table 2.2.6.

A secial mentioning deserve, in this connection, ammonia and primary lower aliphatic amines as swelling media for cellulose. Liquid ammonia and low aliphatic primary amines are able to penetrate into the crystalline regions of the cellulose. They promote an excessive swelling and a change in the lattice dimensions. After suitable procedures for decomposing the addition compound formed and for eliminating the ammonia or the amine from the cellulose moiety, a rather amorphous and highly accessible cellulose sample results. Especially the swel-

ling treatment with liquid ammonia can be considered as one of the most efficient activation procedures for cellulose (see also chapters 2.4 and 4.2).

Higher primary amines are not able to penetrate into the lattice by themselves due to the high molar volume, but can form highly swollen addition compounds after preswelling with a lower amine (Davis et al., 1943; Creely et al., 1959).

Table 2.2.5. Effect of molar volume of swelling medium on swelling of regenerated cellulose in organic liquids (Philipp et al., 1973a)

Swelling medium	Molar volume[a] (cm^3)	Equilibrium LRV (%)	
		Spruce sulfite pulp	Rayon staple
Ethylene glycol	55.7	85	80
Diethylene glycol	95.2	90	25
Triethylene glycol	132	90	21

[a]Defined as molar mass divided by density.

Table 2.2.6. LRV of cellulose in hydroxygroup- and in aminogroup-containing liquids

Swelling medium	Equilibrium LRV (%)					
	Cotton	Hydrol. linters	Spruce untreated	sulfite pulp decryst.	mercerized	Rayon staple
Ethylene glycol	57	41	84	95	90	80
Ethylene diamine	127	99	137	157	134	148
Ethanol	21	14	32	23	29	20
n-Propylamine	52	18	53	77	100	86

Swelling of cellulose in a liquid of high swelling power with subsequent liquid exchange to a liquid of lower swelling power often results in retaining a very high swelling value also with the second liquid, as demonstrated by examples in Table 2.2.7. A procedure of this kind can also be used efficiently for activating a cellulose sample for a subsequent reaction in a liquid of rather low swelling power.

The strong influence of cellulose structure on the equilibrium swelling value can be derived too from the data presented already in Table 2.2.7. Among native cellulose samples, cotton and cotton linters generally show a lower swelling than wood pulp. By a decrystallizing pretreatment, for example with liquid ammonia, the swelling can be enhanced considerably. Comparing cellulose I (native cellulose) and regenerated cellulose (cellulose II), the latter obviously has a higher

equilibrium swelling value in strongly swelling agents of rather small molar volume, e.g. water or formamide.

Table 2.2.7. Retainment of cellulose swelling after change of swelling medium (Wagenknecht, 1976)

	LRV (%)	
	Cellulose samples (preswelling in ethanolamine)	
Subsequent swelling in	Cotton 106 %	Rayon cord 258 %
DMSO	108	285
DMF	81	111
Ethanol	56	94
	Cellulose samples (preswelling in water)	
Subsequent swelling in	Cotton 51 %	Rayon cord 69 %
DMSO	88	195
DMF	61	53
Ethanol	29	29

An increase in molar volume at rather constant polarity and hydrogen-bond-forming tendency often leads to a decrease of swelling in the case of cellulose II samples due to the before-mentioned hindrance of liquid penetration into the pore system of the sample, which exhibits a different pore morphology compared with native cellulose (see Table 2.2.5). Within the class of cellulose II samples, the equilibrium swelling value depends decisively on fiber or film morphology.

Most of the swelling processes of cellulose proceed very fast, within minutes. This holds true especially for samples of native cellulose in most of the swelling agents used today, as well as for samples of regenerated cellulose in protic liquids of high swelling power, like water or ethanolamine. With several aprotic liquids of medium to high swelling power, however, a rather low rate of swelling is observed in some cases with the retardation depending on the structure of the cellulose II sample. This peculiar behavior was observed especially with DMSO and also with pyridine, and it took days or even weeks before a final swelling value had been reached: an effect to be considered in preswelling of cellulose II in these media prior to a derivatization. The different behavior of cellulose I and cellulose II structure in formamide on the one hand, and DMSO on the other, is illustrated in Fig. 2.2.6 (Philipp et al., 1973b). A kinetic interpretation of these rather complex swelling curves of cellulose II in DMSO, which often show a pronounced induction period, is given by Hartwig et al. (1987).

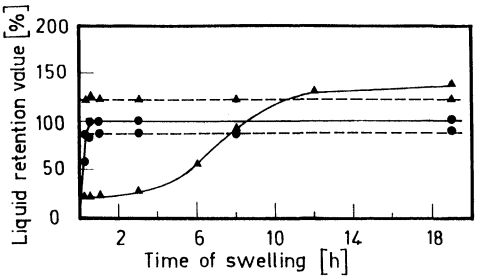


Figure 2.2.6. Liquid retention value (LRV) versus time of swelling of cellulose in DMSO (▲) and formamide (●): broken line, spruce sulfite pulp (cellulose I); solid line, rayon staple fiber (cellulose II) (Philipp et al., 1973b).

In connection with the influence of cellulose structure on rate and final state of swelling, the influence of the temperature and the final state of sample drying has to be mentioned too (see Fig. 2.2.7). A change from a never-dried sample to a dry sample prepared at room temperature, already decreases the equilibrium swelling value considerably, not only in the case of water as the swelling medium. With increasing temperature of drying, a further decrease in swelling value is observed which becomes more pronounced at temperatures above 130 °C. Most affected by the state of drying, as well as by the physical structure of the sample in general, is the swelling in DMSO (Schleicher et al., 1974). The swelling curves of liquid retention value (LRV) versus swelling time can conveniently be used to indicate even small changes in sample structure or changes in the state and procedure of drying (Hartwig et al., 1987).

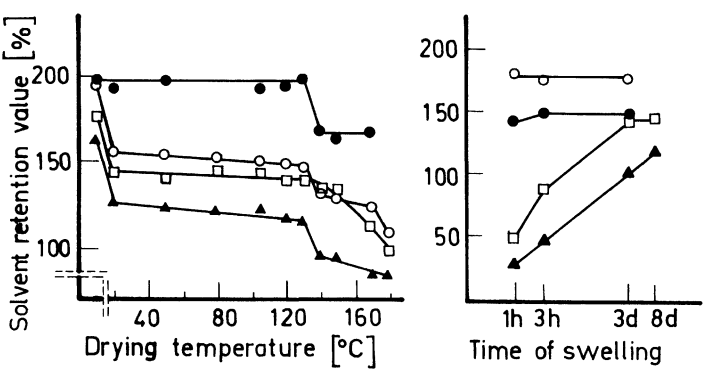


Figure 2.2.7. Effect of drying on the course of swelling in DMSO. Left: ● viscose, ○ pulp, □ alkali cellulose, regenerated, ▲ pulp, hydrolyzed; right: ○ alkali cellulose, regenerated, never dried, ● dried 8 h at 20 °C, 65 % relative humidity, □ dried 2 h at 105 °C, ▲ dried 1 h at 180 °C (Schleicher et al., 1974).

2.2.1.3 Swelling of cellulose in aqueous solutions of sodium hydroxide and in related systems

The swelling of cellulose in aqueous solutions of sodium hydroxide has been observed already about 150 years ago and has since been the topic of a large number of experimental investigations and theoretical considerations. These were stimulated by the high practical relevance of the interactions occurring in the systems cellulose/sodium hydroxide/water, in changing the properties of textile cellulose fibers by the so-called mercerization process, as well as in preparing the cellulose for a subsequent chemical reaction by the preceding formation of alkali cellulose.

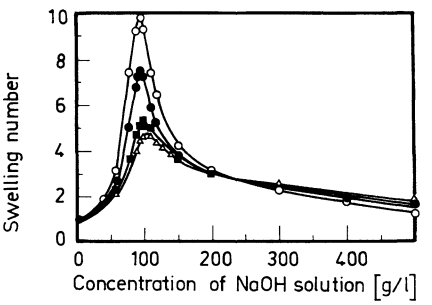


Figure 2.2.8. Swelling number (derived from increase in cross-section) of rayon in aqueous NaOH: ○ 14 °C, ● 20 °C, ■ 25 °C, Δ 31 °C (Saito, 1939).

Systematic investigations (Heuser and Bartunek, 1925; Saito, 1939) during the first decades of the century already revealed three important phenomena of cellulose swelling in aqueous alkali, i.e.
(i) the passing of the swelling value through a maximum in dependence on lye concentration (see Fig. 2.2.8);
(ii) a qualitatively similar but quantitatively different behavior of all the alkali hydroxides in aqueous solution from LiOH to CsOH on interaction with cellulose in an aqueous medium;
(iii) a phase transition within the regions of crystalline order above a lye concentration of 12–15 % due to a so-called intracrystalline swelling caused by inclusion of NaOH and H_2O into the crystallites.

Swelling of cellulose in aqueous alkali generally proceeds very rapidly. The increase in thickness of a pulp sheet after immersion in aqueous NaOH reached its final value within a few minutes, following the rate law (Schwabe and Philipp, 1954, Q is degree of swelling in thickness):

$$Q = \frac{a \times t}{1 + b \times t} \quad \text{or} \quad \frac{dQ}{dt} = k(Q_\infty - Q)$$

$$\text{with } k = b^2/a \text{ and } Q_\infty = \text{equilibrium value}$$

The swelling maximum depends with regard to its height and its position on the concentration axis, somewhat on the physical structure of the sample, and is shifted to higher lye concentration in the order: beach sulfite pulp, spruce sulfite pulp, cotton linters. A lowering of the swelling temperature in the range of technical interest, between +50 and –10 °C, generally results in an increase of height of the swelling maximum, whereas the rate of swelling is effected to a small extent only.

The swelling of cellulose in aqueous NaOH is just one, but a very important, phenomenon encountered in the very complex process of cellulose–alkali interaction (see chapter 4.2), which affects all three levels of the cellulose structure. On the molecular level a strong chemical interaction takes place between cellulosic hydroxy groups and the NaOH ion dipoles, resulting in cleavage of inter- and intramolecular hydrogen bonds. On the supramolecular level, a change in lattice dimensions and chain conformation occurs in a range of lye concentration near the swelling maximum, and the overall lateral order is significantly decreased in this process, but still kept at a rather high level. The inter- and intracrystalline swelling of the fiber structure in NaOH results in a different composition of the disordered and the crystalline parts of the alkali cellulose. Also, on the morphological level, rather drastic changes in fibrillar architecture can take place on interaction with aqueous alkali.

For understanding the swelling of cellulose in aqueous NaOH, in dependence on lye concentration, the existence of defined hydrates of the NaOH ion dipoles is essential, the hydration number of which decreases stepwise with increasing lye concentration. Already in the low concentration range, the clustered water structure is disturbed by the hydrated alkali ions, resulting in the formation of so-called 'monomolecular' water as a constituent of the system (Bartunek, 1953; Dobbins, 1970). The penetration of this monomolecular water into the cellulose structure paves the way for further swelling by destroying intermolecular hydrogen bonds, and facilitates the entrance of hydrated ion dipoles into the structure. The degree of swelling can then be considered as being determined by two factors, i.e. the number of water molecules conveyed into the cellulose structure by each of the alkali ions or ion dipoles, which decreases with increasing lye concentration, and the depth of penetration of these ion dipoles into this structure, which increases with lye concentration, until even the highly ordered regions are transformed to alkali cellulose. The existence of a swelling maximum can then be understood by the counteraction of these two factors: at low alkali concentra-

tion the second factor is the prevailing one and swelling increases with lye concentration, whereas after complete penetration of the whole structure, the decline in hydration number with increasing concentration is the decisive point leading to lower swelling values beyond the maximum. By this reasoning also, the swelling maximum in aqueous KOH can be explained, which occurs at about the same molar lye concentration of 4 M, but is only half as high as that observed with NaOH, obviously due to a much lower hydration number caused by the higher ion radius and the changed electron configuration. Besides the simple qualitative model presented here on the basis of distinct alkali hydroxide hydrates, several other concepts for explaining the course of swelling with alkali concentration have been published, which, however, are not contradictory, but supplementary to that outlined here. These other concepts will be discussed in some detail in chapter 4.2.

In contrast with the comprehensive work with aqueous solutions in studying the swelling of cellulose by alkali hydroxides, results obtained with nonaqueous solutions are rather scarce. From experiments with NaOH dissolved in aliphatic alcohols, it can be stated that swelling is markedly reduced in comparison with aqueous systems, and proceeds much more slowly.

2.2.1.4 Interaction of cellulose in media in the transition range between solvent and swelling agent

In dependence on composition of the system on one hand, and on the *DP* and the physical structure of the cellulose sample on the other, aqueous and nonaqueous systems can frequently act on cellulose either as a solvent or as a swelling agent, effecting a limited swelling only. Furthermore, due to the polydispersity and morphological heterogeneity of most of the cellulose samples employed, interaction with numerous of these systems results in a partial dissolution of the sample and a more or less large, highly swollen, solid residue. The phenomena outlined here in a general manner are especially encountered with binary systems containing an active component and a more or less inert solvent. The following examples are intended to illustrate these general and rather abstract considerations.

Well-known metal-complex solvents for cellulose like Cuam, Cadoxen or FeTNa (see chapter 4.3) can be modified rather simply to agents for a limited swelling just by lowering the concentration of the active metal complex, and have been used rather frequently as media for morphological investigations on cellulose swelling (Casperson et al., 1969). The binary aprotic, organic solvent system dimethylacetamide (DMA)/LiCl (see section 2.2.2 below) acts as a solvent only above a critical concentration of the complex-forming salt, and in the case of highly ordered high *DP* cellulose, only after a suitable pretreatment for enhancing the accessibility of the sample. Figure 2.2.9 shows the increase of

solvent power of binary mixtures of DMSO and *N*-methylmorpholine-*N*-oxide (NMMNO) with increasing ratio of the active component NMMNO to DMSO, and demonstrates simultaneously the tremendous effect of cellulose physical structure in dissolution and swelling: a 20:80 mixture dissolves completely a decrystallized cellulose sample obtained by NH_3 pretreatment, whereas an untreated sample is dissolved only to a minor extent.

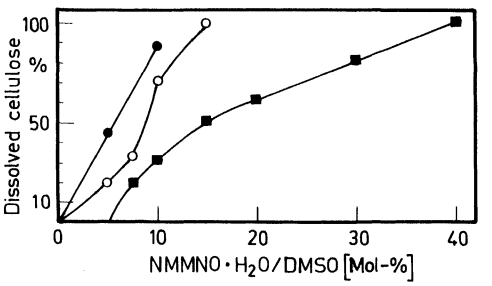


Figure 2.2.9. Effect of crystalline order of cellulose on its solubility in NMMNO/DMSO mixtures: ■ beech, ○ beech-NH_3, ● beech, reprecipitated (Berger et al., 1989).

The transition from a swelling agent to a solvent has been very obviously demonstrated in an earlier publication of one of the authors (Schwabe and Philipp, 1955) by the example of aqueous solutions of tetraethylammonium hydroxide. As detailed in chapter 4.2, aqueous solutions of this quaternary ammonium base caused a rapid limited swelling, up to a concentration of about 1.7 M, while at or above 1.8 M, an unlimited swelling, i.e. a complete dissolution of the fiber structure, occurred with the spruce sulfite pulp employed.

Finally some more comments on the interaction between cellulose and aqueous sodium hydroxide in the transition range between limited swelling and dissolution seem appropriate, also with regard to the practical importance for cellulose processing and derivatization. It has been well known for many decades that on interaction between aqueous NaOH and cellulose a limited part of the polymer is dissolved, the amount depending on lye concentration as well as on cellulose structure, and being composed mainly of easily accessible short cellulose chains and hemicelluloses. In dependence on lye concentration, the maximum of solubility coincides widely with that of limited swelling of the insoluble part, and is situated at a lye concentration of about 10 % by weight. The amount dissolved at this concentration covers the range between 1 % with high-viscosity cotton linters and highly refined dissolving pulps, to 10 % with conventional spruce or beech-dissolving pulps.

A rather complete solubility in 10 % aqueous NaOH is observed with viscose rayon after acid hydrolysis to the level-off *DP* of 30–40 or with xylans obtained by alkaline extraction from beech wood or wheat straw.

The solubility of cellulose samples in aqueous NaOH can be significantly enhanced by adding zinc oxide or urea to the system and/or by lowering the temperature of the treatment. Addition of zinc oxide leads to an *in situ* formation of a zincate complex facilitating dissolution of cellulose chains up to a *DP* of about 200, even at room temperature. This route has been employed to assess the short-chain part of dissolving pulps (Bergner and Philipp, 1986). The effect of urea can be understood by a breaking of the clustered water structure enhancing the content of free monomolecular water, which promotes swelling and dissolution of the polymer. The increase in solubility by lowering the temperature of the system is in agreement with an exothermic heat of dissolution, and has been investigated thoroughly in recent years with regard to a possible fiber spinning from cellulose/NaOH solutions at low temperature (see also chapter 4.2).

2.2.2 Dissolution of cellulose

2.2.2.1 Some general comments on cellulose dissolution

Until about 1950, only Cuam was well-known and widely used as a solvent for cellulose. Besides this, aqueous solutions of the cupriethylene diamine complex and of selected tetraalkylammonium hydroxides were employed to a minor extent as solvents for analytical purposes. About 10 years later the spectrum of cellulose solvents was considerably broadened by the discovery of numerous further metal-complex solvents employing transition metal atoms as the center of the complex. Special regard must be given here to the work of Jayme and his group (Jayme, 1978) for their achievements in discovering and introducing solvent systems like FeTNa and Cadoxen into cellulose research and development. In the following decades the situation changed completely in so far as a host of organic solvent compositions for cellulose was discovered and described by numerous research groups all over the world, especially by Japanese, US-American and German researchers. A strong impetus to this development was given by the striving for alternative processes for the manufacture of cellulosic manmade fibers, which promised a better environmental compatibility than the classical viscose process. Especially these organic solvent systems, with many aprotic systems among them, also opened up new approaches to homogeneous cellulose derivatization in various organic media.

Several proposals have been made in recent years for a systematization of the vast number of solvent systems known today. From the viewpoint of the organic chemistry of cellulose, a classification according to the two categories of nonderivatizing and of derivatizing solvents is considered most appropriate and will be used in the following context. The term 'nonderivatizing solvent' denotes systems dissolving the polymer by intermolecular interaction only. Aqueous metal transition-complex solvent systems are conveniently included in this cate-

gory despite an often very strong interaction, as no covalent derivatization occurs. The group 'derivatizing solvents', on the other hand, comprises all the systems where dissolution of cellulose occurs in combination with the covalent derivatization to an unstable ether, ester, or acetal. A specification within the large group of systems derivatizing cellulose with a change from a heterogeneous to a homogeneous system, is given by the criterion that the derivative formed in a so-called derivatizing solvent system is easily decomposed to regenerated cellulose by changing the medium or the pH-value of the system. Both categories of solvent systems comprise aqueous as well as nonaqueous compositions.

Before presenting a systematic description of important solvent systems for cellulose, a brief comment shall be given on the analytical procedures suitable for investigating cellulose dissolution with regard to changes in chemical and physical structure during this process.

On the level of the gross structure of cellulose fibers, the determination of the insoluble residue under different conditions or stages of dissolution is still a convenient and widely used method which, however, is seriously limited in the region of low residue values. In the case of very low residues the assessment of a filtering or clogging value can be a useful tool for evaluating the quality of a cellulose solution with regard to absence of fiber fragments and gel particles, as widely practised with technical viscose spinning dope. Changes in cellulose fiber morphology in the course of dissolution have been successfully investigated in recent years by imaging single cellulose particles during their flow through a capillary installed in the solvent system via a light-scattering technique and subsequent signal evaluation. This morphometric technique, developed by Unger (1985), will be considered in some detail in chapter 3.

The supramolecular state of solution finely achieved, i.e. the persistence of native fragments as well as the formation of secondary aggregates, has been investigated by a variety of instrumental techniques, such as centrifugation and ultracentrifugation gel particle counting turbitity measurements, or light scattering, the latter obviously being preferred for obtaining quantitative information on polymer chain aggregates present in a macroscopically clear solution.

On the molecular level, the most relevant question is whether or not a covalent derivatization takes place during dissolution. High-resolution liquid-state NMR spectroscopy, especially ^{13}C NMR, proved to be a powerful tool (Nehls et al. 1994). A further problem encountered on the molecular level is the question of polymer degradation during the dissolution process, for example by hydrolytic chain cleavage. Quantitative information can be obtained by common methods of molecular weight determination, as e.g. GPC. For a qualitative comparison of samples or procedures, simple viscosity measurements are widely used, but a quantitative interpretation of results obtained should be handled with caution.

2.2.2.2 Systematic description of important classes of cellulose solvent systems

This subsection will be structured according to nonderivatizing and derivatizing solvent systems, covering in each category aqueous as well as nonaqueous ones, and including also some comments on the mechanism of dissolution for practically or scientifically relevant systems.

The transition metal-complex solvent systems are added to the category of nonderivatizing solvents as a special group.

Nonderivatizing organic solvents for cellulose

Due to their relevance for the organic chemistry of cellulose under homogeneous conditions, the numerous solvents employing an organic liquid as medium or active component shall be considered first and in some detail before turning to aqueous solutions of some bases and of transition metal complexes showing solvent action on cellulose.

From an historical point of view, combinations of some simple inorganic compounds, i.e. of SO_2, NH_3, and a suitable ammonium salt, can indeed be considered as the origin of two large groups of nonderivatizing solvent systems, and also the inorganic compound N_2H_4, i.e. water free hydrazine has been described as an efficient also somewhat exotic solvent for cellulose (Litt and Kumar, 1976). The first group to be mentioned comprises a large number of systems containing SO_2 in combination with aliphatic amines and a suitable polar organic liquid (Nakao, 1971; Hata and Yokota, 1966a and 1966b). The sulfur component may be modified by employing $SOCl_2$. As an amine component diethylamine has been used in most of the relevant publications. Suitable polar liquids employed as the third component are for example DMF, DMSO, DMA, or formamide. The interaction of these solvent systems with cellulose can be understood as an electron donor acceptor interaction according to the scheme shown in Figure 2.2.10. But also a transition to some kind of covalent interaction may occur.

The SO_2-containing systems obviously have no chance of technical realization due to the aggressiveness of SO_2, but they have been used successfully for special derivatizations under homogeneous conditions, e.g. benzylation of cellulose.

The second group of solvent systems considered here consists of an amino-group-containing active component in a suitable polar organic liquid with a further component such as ethanolamine and/or a suitable inorganic salt like sodium bromide being added to facilitate cellulose dissolution (Schleicher et al., 1972). This group of solvents therefore exhibits a very broad spectrum with regard to chemical composition, without a clear cut systematization and interpretation of chemical binding forces being possible up to now. This whole group

can be traced back to early studies on the solvent action of liquid ammonia in combination with some inorganic salts (Scherer, 1931). As a rather simple and well-understood example, the binary mixture DMSO/methylamine may be mentioned here. This is a borderline solvent of limited power, as only native cellulose of low to medium *DP* can be transformed to a clear, fiber-free solution. A scheme of the electron donor–acceptor (EDA) interaction, discussed here as the driving force for dissolution, is presented in Fig. 2.2.11 (Philipp et al., 1977).

Another group of nonderivatizing organic solvent systems for cellulose, which has to be considered today as the most relevant one with regard to practical use, takes advantage of the strong intermolecular interaction between the polymer and some dipolar aprotic organic compounds with N→O or C=O dipoles.

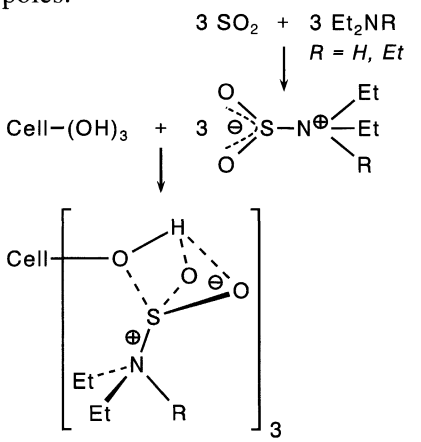


Figure 2.2.10. Interaction of cellulose with the system SO_2/amine/organic liquid (Isogai, 1987).

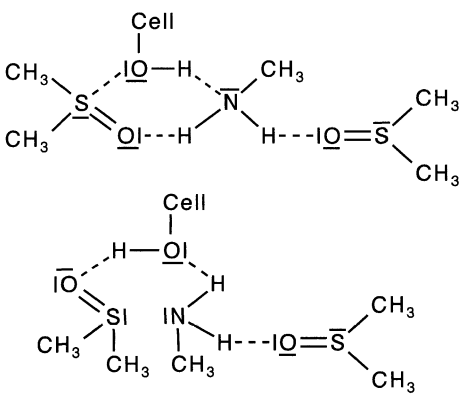
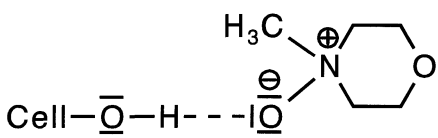


Figure 2.2.11. EDA interaction of cellulose with the system DMSO/CH_3NH_2 (Philipp et al., 1977).

From the experimental point of view, as well as with regard to the interaction mechanism, this class of solvents has to be subdivided into the two groups of salt-free and salt-containing systems, the latter generally employing LiCl as an additional component with rather high solubility in the dipolar aprotic compound. A survey of salt-free systems, with NMMNO being the most important representative, is listed here.

- Aqueous tetraalkylammonium hydroxide of higher molar volume and high concentration, e.g. diethyldibenzylammonium hydroxide
- *N*-oxides of tertiary amines of special constitution, e.g. NMMNO · 1 H_2O, triethylamine-*N*-oxide or *N*,*N*-dicyclohexylmethylamine-*N*-oxide
- Anhydrous hydrazine
- Methylamine/DMSO
- *sec./tert.* aliphatic amine/SO_2
- NH_3/SO_2/DMSO or formamide
- Ethylenediamine/SO_2/DMSO
- *sec./tert.* amine/SO_2/polar aprotic liquid
- *sec./tert.* amine/$SOCl_2$ or SO_2Cl_2/DMSO or formamide

NMMNO and its monohydrate form the base of an alternative process now used for cellulosic manmade fiber manufacture, which is practised already on a technical scale. NMMNO · 1 H_2O dissolves even high *DP* cellulose rather quickly at a temperature of about 85 °C to a clear melt solution. The aminoxide can be diluted with an aprotic compound like DMF or DMSO down to a ratio of about 1:1 without losing its solvent power (Kabrelian et al., 1988 and 1989). The interaction between NMMNO and cellulose can be interpreted as a hydrogen-bond-complex formation with a superimposed ionic interaction according to Maia and Perez (1983):



Moreover, water is included in the EDA interaction between cellulose and NMMNO via hydrogen bonds involving the O- and the H-atom of the cellulose hydroxy groups, as well as the H_2O molecule of the NMMNO monohydrate, as the solvent-active species.

In the case of the salt-containing systems, e.g.

- *N*-ethylpyridinium chloride (melt)
- KSCN/DMSO
- NH_3(l)/NH_4SCN; NaSCN; $NaNO_3$; NaI; NH_4I; tetraethylammonium bromide
- DMA/LiCl
- *N*-methylpyrrolidone/LiCl
- Hexamethylphosphoric acid triamide/LiCl
- NH_3/NaBr/ethanolamine; morpholine; formamide; DMSO
- Ethylenediamine/NaI/DMF
- LiCl/pyridine; chinolin
- Tetraalkylammonium halides/DMSO

a direct complexation between the cation and the cellulosic hydroxy group has to be assumed. One of the structures proposed is depicted in Fig. 2.2.12 (cf. chapter 4.3; El-Kafrawy, 1982).

A system of high relevance for cellulose etherification and esterification under homogeneous conditions within this group is DMA/LiCl (see chapter 4.7). After preactivation, even high molecular cellulose can be dissolved without residue and detectable chain degradation. This can be considered as an important asset of this solvent for analytical purposes, as well as for homogeneous cellulose derivatization (see Appendix in volume II).

Cellulose dissolution without covalent derivatization in general can be understood as an acid–base interaction with the amphoteric cellulose taking the role of either the acid or the base in dependence on the solvent structure (Turbak et al., 1980). In our opinion this acid–base concept may be useful in connection with aqueous solvents, but obviously is of minor relevance in connection with organic solvents of limited polarity or ionizability. Nakao (1971) and later Schleicher (1983a, b) proposed an electron donor–acceptor interaction as the driving force of many dissolution processes of cellulose in organic systems, assuming a participation of the O-atom as well as of the H-atom of the cellulosic hydroxy group with the same or with different compounds of the solvent. A general scheme of this model is presented in Fig. 2.2.13.

An advantage of this model is its general applicability which on the other hand diminishes its heuristic value, and additional assumptions are necessary to adopt it to special classes of solvent systems. A model published by Berger et al. (1990) is centered on the formation of so-called crypto-ionic hydrogen-bonds between cellulose and solvent components and includes energetic considerations with regard to interchain and chain–solvent interaction. Due to its conciseness it can be helpful as a guideline in the experimental search for new solvent systems

but obviously is limited in applicability, predominantly to dipolar aprotic solvent systems.

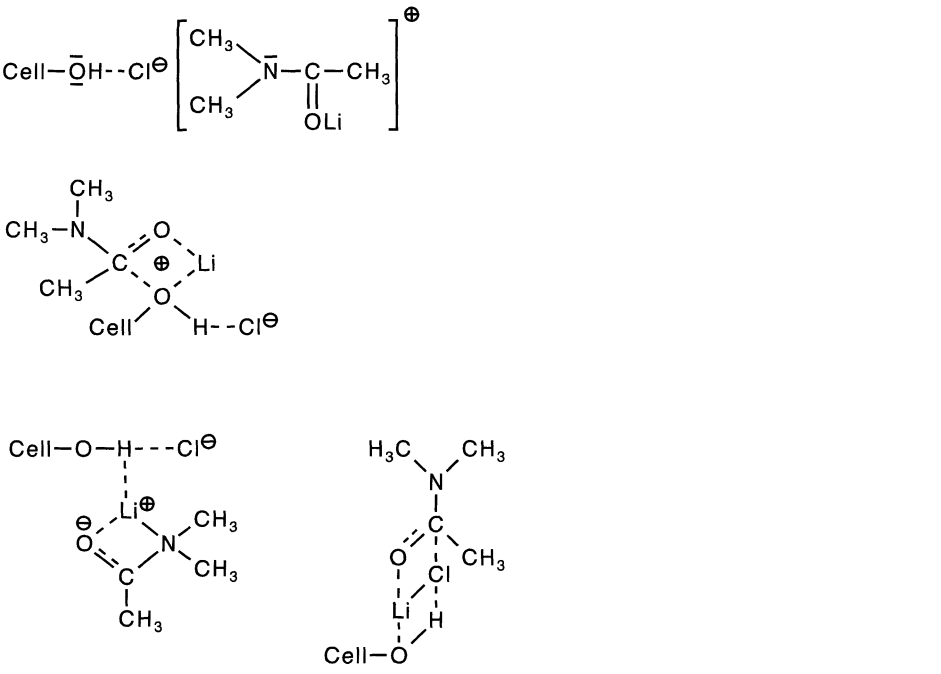


Figure 2.2.12. Scheme of interaction of cellulose with DMA/LiCl (Dawsey an McCormick, 1990).

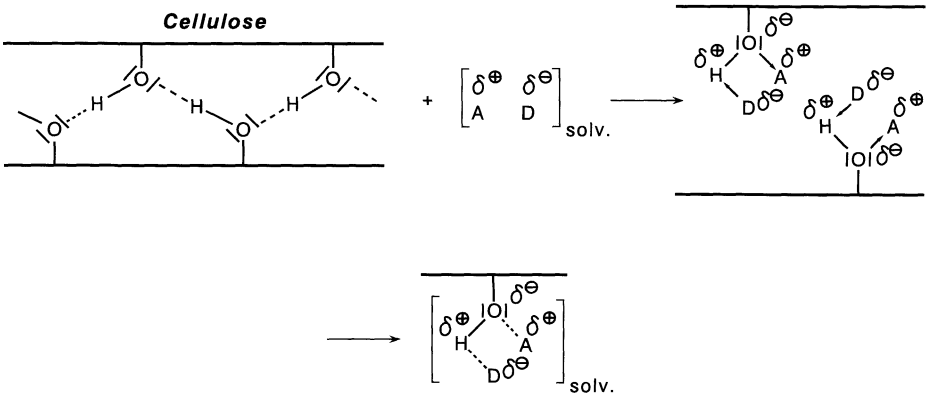


Figure 2.2.13. Schematic EDA interactions between cellulose and a nonderivatizing solvent (Philipp et al., 1978).

Ionic compounds in aqueous solution as cellulose solvents

It has been known since the first decades of our century that some inorganic acids, strong bases, and some inorganic salts in concentrated solution can act as cellulose solvents of limited solvent power. Especially in the case of acids and concentrated salt solutions at higher temperature, the dissolution is accompanied by a severe chain degradation, limiting further the practical relevance of these classes of solvent. Studies on cellulose dissolution in melts of rhodanites or rhodanite hydrates (Lukanoff et al., 1983) broaden the spectrum of this group of 'cellulose solvents', but simultaneously confirm the above statement of chain degradation.

Only a small number of all these compounds reported to dissolve cellulose are of a real practical interest in cellulose chemistry. Aqueous phosphoric acid with an acid content of about 85 % has long been known as a solvent for cellulose and has been used for analytical purposes, as well as a medium for homogeneous oxidation of this polymer (Heinze et al., 1993). As shown by ^{13}C NMR experiments (Nehls et al., 1995), some derivatization to a phosphoric acid ester of cellulose occurs in this process of dissolution, but it is still an open question whether this esterification with a hydrophilic anionic group or an acid–base interaction with unsubstituted hydroxy groups is the main course of cellulose solubility in this system.

The solvent action on cellulose of some tetraalkylammonium hydroxides in concentrated aqueous solution, like dimethylbenzylphenylammonium hydroxide or triethylbenzylammonium hydroxide, which is caused by the spacer action of the voluminous cation, will be considered in more detail in chapter 4.2.

Aqueous solutions of transition metal complexes as solvents for cellulose

Solvents of practical relevance for analytical application are the copper complexes with ammonia (Cuoxam) and ethylenediamine (Cuen), the cadmium complex with ethylenediamine (Cadoxen), and the ferric tartaric acid complex in alkaline aqueous solution (FeTNa). All of these four complex systems are able to dissolve cellulose even of high *DP* completely without residue, the nitrogen-containing complexes being rather quickly, the ferric tartaric acid complex more slowly. The cuprammonium complex had been employed in the past as a medium for homogeneous derivatization reactions of cellulose, for example methylation, but is now replaced generally by nonderivatizing or derivatizing organic solvents, which are more convenient to handle in subsequent synthesis. Recent progress obtained by the work of Klüfers and co-workers (Kettenbach et al., 1997) in understanding formation and properties of these complexes will be considered in detail in chapter 4.3. According to ^{13}C NMR experiments (Nehls et al., 1995), the strength of interaction between the cellulosic hydroxy groups and the metal complex can differ rather greatly: in the case of Cadoxen no chemical shift due to interaction with the complex could be observed and the

^{13}C NMR spectrum resembles to that of cellulose in aqueous sodium hydroxide, whereas the cellulose spectrum in FeTNa indicates a very strong interaction, by a considerable chemical shift, of all the C-atoms.

Derivatizing solvent systems for cellulose

In contrast with many of the nonderivatizing solvents considered above, the chemical interaction between cellulose and solvent on the molecular level is rather well-defined and well understood in the case of most derivatizing solvent systems. Open questions still arise in connection with the interference of the hydrogen-bond system along and between the polymer chains on the course of the simultaneous derivatization and dissolution, and also with regard to the course and state of solvation of the substituted and nonsubstituted sites within the anhydroglucose units by the surrounding medium.

A selection of nonaqueous as well as aqueous derivatizing solvent systems and the reaction scheme of the derivatization process are presented in Table 2.2.8; solvents of interest for a subsequent consecutive derivatization are marked with an asterisk.

Table 2.2.8. Examples of aqueous and non-aqueous derivatizing and solubilizing systems for cellulose

System	Cellulose derivatives formed
H_3PO_4 (> 85%)/H_2O	Cell-O-PO_3H_2
HCOOH/e.g. $ZnCl_2$	Cell-O-(O)CH
$CF_3COOH/CF_3(CO)_2O$*	Cell-O-(O)CCF_3
N_2O_4/DMF*	Cell-O-N=O
Me_3SiCl/e.g. pyridine*	Cell-O-$SiMe_3$
$(CH_2O)_3$/DMSO	Cell-O-CH_2OH
CCl_3CHO/DMSO/TEA	Cell-O-CH(OH)-CCl_3
CS_2/NaOH/H_2O	Cell-O-C-(S)-SNa

The three acidic systems, i.e. concentrated formic acid in the presence of $ZnCl_2$ or H_2SO_4 as a catalyst (Takahashi et al., 1986), trifluoroacetic acid (Gedes, 1956) and N_2O_4/DMF (Fowler et al., 1947) are able to dissolve even high *DP* cellulose, which is accompanied, however, by a more or less severe hydrolytic chain degradation. Therefore, trifluoroacetic acid is used frequently for simultaneously dissolving and hydrolyzing cellulose samples. This process is accompanied by a rather slow derivatization to the appropriate cellulose ester, at first in the 6-position, and later in the 2- and 3-position, with the rather unstable trifluoroacetic acid ester groups being decomposed in the subsequent steps of the hydrolysis procedure in the presence of water.

The solvent N_2O_4/DMF forming cellulose nitrite during the dissolution process, dissolves even high *DP* cellulose without any pretreatment very quickly, i.e. within minutes. About 20 years ago this medium was therefore considered for manufacturing artificial cellulose fibers, as well as for subsequent derivatizations via the very unstable and mobile nitrite group (Schweiger, 1979). Using this system even at the laboratory-scale toxicological hazards due to formation of nitrous amines by nitrosation of dimethylamine liberated from the DMF have to be considered. For many years a controversial discussion took place on whether a covalent derivatization or just the formation of an addition compound takes place. Recently this controversy could be settled by joint chemical experiments and *in situ* ^{13}C NMR measurements (Wagenknecht et al., 1992) showing that under strictly anhydrous conditions, cellulose trinitrite is formed. The nitrite groups in the C-6 position proved to be much more stable than those in the C-2/C-3 position against for example hydrolysis by traces of water. This is to be kept in mind in employing this system for subsequent derivatizations. According to experience in the authors group the water content has to be maintained at the very low level of about 0.01 % in order to get reproducible results of cellulose dissolution and subsequent derivatizatio. At a water content of about 0.1 %, dissolution can already be incomplete and hydrolytic chain degradation increases considerably. Obviously most of the derivatizing, as well as some non-derivatizing, organic solvents are very sensitive to water and therefore require careful control of the water content in handling, but the N_2O_4/DMF system can be considered as a rather extreme example here.

Finalizing this discourse on derivatizing solvents of an acidic nature, a brief comment seems to be appropriate on the combined dissolution/acetylation of cellulose in a mixture of acetic anhydride and a dipolar aprotic liquid like DMF or DMSO in the presence of a catalyst. Solvents of this kind of course do not belong to the derivatizing systems according to the definition given above, as a rather stable cellulose ester is obtained. But partially substituted organo-soluble cellulose acetates can be used with advantage as intermediates in subsequent homogeneous derivatizations with the protecting acetate group being easily split off by alkaline treatment (Wagenknecht, 1996).

A combined dissolution/derivatization of cellulose via formation of rather unstable silyl ethers of cellulose, by employing a trimethylsilyl chloride as the active reagent, can be accomplished along two routes, i.e.

(i) by reacting the sample with trimethylsilyl chloride in a medium of low polarity in the presence of pyridine as a base, binding the HCl formed and arriving at a solution of a trimethylsilyl cellulose with a degree of substitution of about 2.5;

(ii) the reaction of cellulose with trimethylsilyl chloride in DMF as a rather polar medium in the presence of ammonia, previously employed for cellulose activation, and arriving at a DMF solution of trimethylsilyl cellulose with a medium

degree of substitution of about 1.5 (Klemm and Stein, 1995; Klemm et al., 1995; cf. chapter 4.5).

Dissolution and derivatization of cellulose in this silyl system takes place more slowly than in DMF/N_2O_4 but has the advantage of a rather small chain degradation, and of the possibility to isolate and purify the silyl cellulose before employing it as an intermediate for further derivatization.

These steps of isolation and purification serve the purpose of separation of the silyl ether from side products like ammonium chloride or hexaalkyl disiloxane formed during the reaction. The control of the water content of the reaction medium is a decisive point also in silyl ether formation. The solubility of trimethylsilyl cellulose in different organic liquids is determined by the degree of substitution (*DS*), as demonstrated by the data given in Table 2.2.9.

Table 2.2.9. Effect of degree of trimethylsilyl groups (DS_{Si}) on the solubility of trimethylsilylcellulose in organic liquids (according to Klemm et al., 1990)

Liquid	Range of solubility DS_{Si}
Ethanol	0.2–0.7
DMSO	0.3–1.2
DMF	0.9–1.7
Acetone	1.6–1.8
Tetrahydrofuran	1.7–3.0
n-Hexane	2.5–3.0

Acetalization of cellulose to organo-soluble products acts as a driving force in dissolution of the polymer in paraformaldehyde/DMSO (Baker et al., 1981) and trichloroacetaldehyde/dipolar aprotic solvent (Seymor and Johnson, 1978). Dissolution proceeds rather fast at higher temperature after suitable preactivation. The acetalization takes place preferentially at the 6 position, and side chains can be formed by subsequent acetalization.

Considering now aqueous systems dissolving cellulose via a covalent derivatization. The combination of CS_2 and aqueous NaOH, leading to a water-soluble anionic cellulose xanthogenate, has to be mentioned first. This xanthation and the subsequent decomposition of the xanthogenate in an acidic aqueous medium, form the chemical basis of the viscose process of manmade cellulose fiber manufacture practised today at a level of about 3 000 000 t annually worldwide. A broad variation of technological procedures is used for xanthation dissolution and thread formation by xanthogenate decomposition. The complicated and exciting chemistry of xanthation, transxanthation, and dexanthation

with their consequences on substituent distribution and state of xanthogenate solutions will be discussed in detail in chapter 4.4. The total *DS* of a freshly prepared viscose solution amounts to about 0.5 and drops to about 0.25 just before spinning. Subsequent homogeneous derivatization reactions can of course be performed only in the surrounding aqueous alkaline medium and are limited to etherification.

As an environmentally more safe alternative to the viscose process, the so-called carbamate method has been developed in order to transform cellulose into artificial fibers via a transient derivatization to a water-soluble but easily decomposable carbamate. The principle of the process consists of the reaction of a suitably activated dissolving pulp with urea, to a cellulose carbamate with a *DS* in the range 0.3–0.4, and a preferential position of the carbamate groups at C-2 (Nuessle, 1961; Segal and Eggerten, 1961). This carbamate is subsequently dissolved in aqueous NaOH with the resulting solution being liable to a moderately fast decomposition into cellulose, sodium carbonate, and ammonia.

The rate of cellulose dissolution in derivatizing solvents, as well as in nonderivatizing ones, varies widely depending on the nature of the solvent and the physical structure of the sample. An especially broad range of dissolution rates is encountered with nonaqueous derivatizing systems, some minutes only being required in N_2O_4/DMF, whereas it may take even weeks before the sample is dissolved in 99 % formic acid. Regarding nonderivatizing systems, no principle differences in rate of dissolution are observed between nonaqueous and aqueous ones, as fast-acting solvents like NMMNO/DMSO or Cadoxen on the one hand, and slow-acting ones like FeTNa and DMA/LiCl on the other, are found in both categories.

The important role of cellulose structure on the rate and completeness of dissolution of a given sample in a derivatizing or nonderivatizing solvent has already been mentioned several times and shall now be considered in some detail. Generally this influence of structure increases with decreasing solvent power of the solvent. This influence is negligible for example with N_2O_4/DMF or with Cadoxen, but the supramolecular structure determines whether or not a sample can be dissolved at all in the case of borderline solvents like methylamine/DMSO.

A decrease in molar mass of the sample frequently leads to a faster rate of dissolution but in the *DP* range of cellulose samples usually employed, this influence is of minor importance with most of the solvents. The deficit of the primary OH group at C-6, realized by employing a linear xylan instead of a cellulose sample of about the same *DP*, seems not to be relevant with aqueous solvents like the transition metal complex systems or the xanthogenate formation, but can decisively decrease the rate of dissolution and even its completeness in the case of nonaqueous derivatizing and nonderivatizing solvents like N_2O_4/DMF or DMA/LiCl.

The supramolecular structure level obviously is of higher relevance in many cases than the molar mass of the sample. Differences in rate of dissolution between cellulose I and cellulose II can occur in several nonaqueous solvents, and in the borderline solvent methylamine/DMSO. The role of crystalline order on the completeness of cellulose dissolution in binary mixtures of NMMNO and DMSO has been demonstrated in Fig. 2.2.9. A content of the active component NMMNO of about 15 mol% already suffices to dissolve completely a decrystallized sample, while about 50 mol% of NMMNO is required in the case of a highly crystalline cellulose of about the same *DP*. The morphological, i.e. the fibrillar, level obviously influences dissolution, especially in some nonderivatizing dipolar aprotic solvents like DMA/LiCl. A suitable preswelling, e.g. in DMA, is a necessary prerequisite here for dissolution at all.

Experimental results, as well as a model consideration on the transition mechanism from the fibrous state to the dissolved one, are still rather scarce and often somewhat contradictory. The assumption of a quick dissolution of all chains from the surface by overcoming interchain connections with a strong chemical driving force poses no problems in the case of a derivatizing solvents like N_2O_4/DMF, acting via the fast formation of a cellulose trinitrite. For nonderivatizing dipolar aprotic media, however, Berger et al. (1988) concluded that the energy of the solvent–cellulose interaction does not suffice to overcome the interchain cohesion by energetic factors alone, and the relevance of an entropic factor is accentuated in publications of these authors. They assume a wedge-like penetration of the solvent into the highly ordered regions of the cellulose structures from the edges or from failure points of the crystallites, resulting in mobilization of chain segments, and thus increasing the entropy of the system. Results obtained with NMMNO or mixtures of this active component with an inert eluent indicate insertion of this solvent into the ordered regions of the sample before dissolution occurs (Berger et al., 1989). Recently a comprehensive comparison was given of the mode of action of FeTNa on the one hand, and DMA/LiCl on the other, employing a spruce pulp and a linters sample in the native as well as the mercerized state, and considering the changes at the different structural levels in the state of partial dissolution of the samples (Piontek et al., 1996). These authors assumed a penetration of the solvent from the fiber surface into the interfibrillar interstices, and predominantly from failure points and edges into the crystallites without a solvent insertion before dissolution. Differences in the mode of action between the two solvents are traced back mainly to a different ratio of swelling ('amorphization') and dissolution rate: in the case of DMA/LiCl the rate of dissolution is assumed to exceed by far that of swelling, and well-defined fibrils of the original shape are found after partial dissolution. In the case of FeTNa, however, an excessive swelling occurs rather quickly followed by a slow dissolution, and a highly swollen fibrillar network is observed by electron microscopy after partial dissolution. With both solvents the influence

of supramolecular structure is considered more relevant than that of molar mass, and especially with DMA/LiCl the decisive role of the morphological level on the course of dissolution is accentuated.

2.2.2.3 Structure formation of cellulose and cellulose derivatives

Solid structure formation of cellulosics as a domain of polymer physics is rather marginal in a text book on cellulose chemistry, but nevertheless shall be considered here briefly in connection with swelling and dissolution. More than 80 % of chemically processed cellulose finds its end-use as a solid polymer material in the form of filaments, films, coatings, membranes, or sorbent agents. This formation of a solid state structure quite predominantly occurs from the highly swollen or dissolved state of this polymer. Besides this, the biosynthesis of cellulose combines the chemical reaction of polycondensation with the formation of a well-defined fibrillar physical structure in a complicated, scientifically exciting process.

Just as with other polymers, solid state structure formation of cellulosics can occur along three routes, i.e.
(i) by bonding or coalescence of the polymer entities in a colloidal polymer dispersion to a coating or a continous film;
(ii) by shaping from the molten or highly softened state with the conventional techniques of thermoplastics processing;
(iii) by solvent evaporation or coagulation from a solution of cellulose or its derivatives, arriving at a filament, film, membrane, particle moiety, or bulk material.

The third one of these routes dominates by far in connection with the chemical processing of cellulose, a combination with one of the other modes being realized in some cases. All three routes can in principle be combined with a chemical conversion, especially of a cellulose derivative as the starting material to a regenerated, nonderivatized cellulose as the final product, as demonstrated by the large-scale conversion of cellulose xanthogenate to cellulose II in the viscose spinning process.

Structure formation from dispersions of cellulosics

Paper sheet formation by interfibrillar hydrogen-bonding between cellulosic OH groups from an aqueous dispersion of highly fibrillated cellulose fibers obtained by wet beating is the most striking and practical most important example for the formation of a continous solid structure from a cellulose dispersion, which, however, shall not be considered further in this book.

Parchmentation by a transient swelling and hydrolyzing action of sulfuric acid and the manufacture of vulcanized fiber as a semi synthetic duroplast by interfibrillar bonding of the fibers in $ZnCl_2$ swollen pulp sheets after subsequent pressing and washing combine the bonding action between the solid entities of a

polymer dispersion with the gluing action of dissolved and reprecipitated cellulosic matter.

Aqueous dispersions of softened cellulose nitrate compete today successfully with the classical nitro lacquers, i.e. solutions of cellulose nitrate in volatile organic solvents by presenting ecological advantages.

Structure formation from the molten or highly soften state

Cellulose itself cannot be processed via the melt state, as the melting point by far surpasses the temperature range of thermal decomposition (compare chapter 2.3). Several highly substituted cellulose derivatives, however, can be processed like thermoplastics, for example by injection molding. This holds true, for example, for benzylcellulose or cellulose butyrate, and also a camphor-softened cellulose nitrate (celluloid) can be shaped by hot pressing (see chapter 4.4).

Thermotropic liquid-crystalline phases, taking an intermediate position between crystalline solid and the isotropic melt, can be prepared from several triesters and triethers of cellulose with sufficiently long side chains. The higher trialkylethers of cellulose, cellulose trialkanoates, and the trialkylesters of tri-*O*-carboxymethylcellulose have been studied in detail (Guo and Gray, 1994), exhibiting melting temperatures and isotropization temperatures in the range between room temperature and about 200 °C, with the melting temperature decreasing with increasing length of the side chains.

Cellulose structure formation from solution

As already emphasized, the route via a polymer solution is by far the most important in solid state structure formation of cellulosics. The large number of parameters that can be chosen independently along this route provides a broad variability of the supramolecular and morphological structure, and provides a fine adaptation of macroscopic product properties to end-use requirements as filaments, films, membranes, or specially shaped particles, but impedes simultaneously the establishment of clear cut correlations between processing, structure, and properties. This holds true even if no covalent chemical reactions are involved and the whole process is controlled by intermolecular interactions only.

Despite this complicated situation, some statements of a more general nature seem to be justified concerning especially the formation of fiber structures but being transferable at least partially also to film structures: the *DP* of the polymer largely determines the level of solution viscosity at a given polymer concentration and thus the tractability of the solution in structure formation. Furthermore, the level of *DP* has a strong bearing on the mechanical properties of the filament or the film, with the breaking strength frequently increasing with the *DP* over a rather wide range. The thermodynamic properties of the solution, which are also of high relevance to the process of structure formation, as well as to product

morphology finally obtained, can be varied within rather wide limits by the solvent chosen for a given cellulose derivative or for cellulose itself. Regarding the state of dispersity of the dissolved polymer, residual structural entities of the starting material can deteriorate processability as well as product quality, while secondary aggregations resulting in preformed structures within the solution may persist throughout the whole process of structure formation with consequences for product structure and properties. Lyotropic phases formed with cellulose itself in solvents like trifluoroacetic acid, NMMNO, or DMA/LiCl, and also with some cellulose derivatives like cellulose acetate or cellulose carbanilate or hydroxypropylcellulose, in some solvents above a critical concentration, deserve special consideration in this connection. Besides the polymer concentration the nature of the substituent, the *DS* and the solvent chosen are decisive parameters for aggregation of the rather stiff polymer chains to liquid-crystalline ordered structures. These systems frequently show very interesting optical properties, opening new approaches for future application, whereas their practical relevance in fiber spinning of cellulosics is still a matter of discussion.

In the process of solid phase formation itself, the route used, i.e. solvent evaporation or polymer precipitation by a nonsolvent, largely determines the type of structure formed, as will be shown in some detail below. The orientation of the polymer chains closely related to several mechanical product properties, takes place to a varying extent already during solid phase formation, but frequently can be still significantly changed by uni- or biaxial deformation ('stretching') in later stages of the process.

Complete evaporation of a volatile solvent from the solution of a cellulose derivative like cellulose acetate or cellulose nitrate usually leads to very dense solid state structures without electron microscopically detectable pores and voids and without well-defined morphological entities like fibrils. This was demonstrated for cellulose acetate films by Purz (1983). By Jones and Miles (1933) the breaking strength of cellulose nitrate films was observed to decrease significantly with the solution viscosity at a given *DS* and a given polymer concentration below a critical level of viscosity or *DP*, respectively, indicating the beginning of a breaking regime by chain sliding. On further reduction of the *DP*, very brittle films were obtained until no continous film formation at all occurred. Chain orientation in films of this type can be significantly increased by mechanical deformation in the solid state. The technical process based on structure formation by solvent evaporation is the so-called dry spinning of cellulose acetate solutions to continuous cellulose acetate filaments which will be abridged briefly in chapter 4.4.

An only partial evaporation of the solvent with subsequent precipitation of the solid phase by a nonsolvent usually results not in dense, but in more or less porous structures, which are of interest for separation membranes in ultrafiltration and reverse osmosis (Kesting, 1985; Purz, 1983). Depending on the system employed and on the mode of preparation, the frequency, size, size distribution, and

shape of the pores can be varied, and can additionally be influenced by the steps of after-treatment (annealing, drying).

Structures formed by coagulation (precipitation) of a solution of cellulose or one of its derivatives with a nonsolvent are characterized by the appearance of fibrils of different size, shape, and regularity as the dominating morphological entities, and a more or less well-defined pore and void structure. Relevant studies have been performed particularly on the mechanism of structure formation from cellulose acetate solutions in connection with the preparation of separation membranes, and on cellulose filament formation by a so-called wet spinning process from a cellulose solution in a nonderivatizing solvent system, especially NMMNO. As shown by Purz (1983), for coagulation structures from cellulose acetate solutions, the process of structure formation is governed by thermodynamic factors, i.e. the interaction parameters between polymer solvent and precipitant, as well as by kinetic parameters determining the velocity of diffusion and mass transport. According to the model developed, the initial step is a droplike demixing into a polymer-rich and a polymer-poor phase, leading subsequently to a three-dimensional network of polymer fibrils, and showing some similarity to lyotropic gel formation. Weak polymer–solvent interaction results in a rather symmetric membrane structure with a uniform cross section, whereas in the case of strong intermolecular interaction, a so-called asymmetric membrane is formed with a cross section exhibiting a structural gradient from one side to the other.

Coagulation of cellulose II from a solution of the polymer in NMMNO by wet spinning is frequently considered today as the most promising future route to filaments and films of regenerated cellulose (Chanzy et al., 1979 and 1980) according to the general scheme:

Slurrying of wood pulp in an aqueous
amineoxide solution (50–60 % NMMNO)
⇓
Evaporation of water at 90–110 °C
under vacuum up to NMMNO · 1 H_2O
(87 % NMMNO/13 % H_2O)
⇓
Melt-solution of cellulose in NMMNO · 1 H_2O
with approx. 10–15 % cellulose
⇓
Extrusion spinning across an air gap into an aqueous spin bath,
with the filament deformation taking place by stretching in the air gap
⇓
Washing and drying of the filament and recovery
of NMMNO by distillation

Regarding the polymer solution, some chain aggregation leading to ordered clustering and a prestructuration of the dissolved cellulose is generally discussed today and frequently assumed. The subsequent shaping of the liquid thread is determined by spinneret geometry, the shearing forces arising in the spinneret, and the subsequent deformation of the liquid thread in the air gap between spinneret and spinning bath. Coagulation to cellulose II proceeds in the spinning bath quickly and rather abruptly ('hard' precipitation) at a spinning velocity of above 100 m/s. This 'hard' coagulation leaves a small margin only for further changes of the fibrillar structure during the passage of the thread through the aqueous spinning bath and in the subsequent steps, in contrast with e.g. the wet spinning of viscose.

The filaments obtained exhibit a smooth surface and a circular cross section. Their microstructure is characterized by a high crystallinity, a high chain orientation in the fiber direction, even in the noncrystalline regions, and 'individualized' fibrils, correlating well to the macroscopic properties of high strength in the dry and wet state, a high modulus, and a tendency to fibrillation on banding.

Formation of the physical structure of the cellulose threads obtained by the "aminoxide process" is comprehensively discussed in (Coulsey and Smith, 1996). The effect of various process parameters on molar mass and molar mass distribution of the polymer has been considered in (Michels, 1998).

A combination of cellulose coagulation with its chemical regeneration from an unstable derivative like cellulose xanthogenate during a wet spinning process increases the number of degrees of freedom and in consequence the variability of product structure and product properties considerably, permitting for example the formation of lobated or serrated filament cross sections or of skin-core filaments in the viscose spinning process. The principles of this large-scale process are described in some detail in chapter 4.4 (Chanzy et al., 1979 and 1980). In subsequent chemical decomposition of a cellulose derivative, solid state structure previously formed from solution can decisively change structure and properties of the specimen too, as demonstrated by the regeneration of cellulose II filaments from a cellulose acetate thread by saponification (see chapter 4.4), or by denitration of a cellulose nitrate film.

Finally it shall be emphasized that obviously some principle differences exist between cellulose solid state structures, especially filament structures obtained on the one hand by wet spinning of the polymer from a solvent system without previous derivatization, and on the other by spinning after previous conversion to an unstable derivative employing the same system and combining coagulation and decomposition. This has been demonstrated by a recent study (Weigel et al., 1996), employing a model spinning system of cellulose dissolved with and without previous derivatization to the trimethylsilylether in the solvent system LiCl/*N*-methylpyrrolidone and using an aqueous spinning bath. As shown by the data in Table 2.2.10, the cellulose threads obtained without intermediate de-

rivatization exhibited a high crystallinity, resulting in a high modulus but a comparatively low loop tenacity similar to those obtained from NMMNO.

Table 2.2.10. Influence of an intermediate derivatization on the properties of solution-spun cellulose filaments (Philipp, 1994)

	Wet modulus (mN/tex)	Rel. loop tenacity (%)	X-ray crystallinity (%)
Viscose	400–1200	95–100	25–35
Silyl/NMP	200–700	60–95	10–15
Silyl/NMP/LiCl	200–700	60–100	10–20
Cell/NMP/LiCl	800–1500	60–80	20–25
Cell/NMMNO	900–5000	40–85	28–45

Rel. loop tenacity: 100 × loop tenacity/filament tenacity, in the dry state; NMP, *N*-methylpyrrolidone; Cell, cellulose, silyl, trimethylsilylcellulose.

After intermediate silylation, on the other hand, the structure and properties of the threads resembled fairly well that of viscose filaments, showing a structure with transition regions between crystalline and amorphous parts, and a broad variability of the mechanical properties, with higher loop tenacity and lower modulus as compared with the model filaments without intermediate derivatization. These findings agree well with earlier results (Lenz et al., 1988) with commercial- or pilot-scale cellulose filaments spun by different processes, indicating a fibril individualization in the case of spinning without intermediate derivatization, but, on the other hand, a trend to fibril twisting and clustering in a combined coagulation/regeneration process.

Table 2.2.11. Process, structure, and property parameters in cellulose structure formation from solution

Process parameters	Structure parameters	Properties
DP, viscosity	Crystallinity	Breaking strength
Concentration of polymer	Size and shape of crystallites	Elongation of break
State of dispersity		Loop tenacity
Polymer solvent interaction	Chain orientation	Permeability to gases, liquids, and colloids
Route to solid state (evaporation, coagulation)	Frequency, size, and shape of pores and voids	Sorption behavior
Deformation during solid phase formation	Shape of cross section	Biodegradability
Steps of after-treatment	Surface structure	Optimal appearance

From a quantitative evaluation of the SAXS pattern of cellulose fibres spun from "derivatizing" as well as from "non-derivatizing" systems, Lenz and Schurz (1990) concluded the existence of clusters of crystallites in the fibre structure, which exhibit an open ramified structure, corresponding to fractal dimensions between 1.2 and 1.8. Fibres spun from non-derivatizing systems, generally had a fractal dimension above 1.4, while fibres obtained from cellulose xanthogenate solutions were located at the low end of the range, in agreement with their assumed more twisted and inter twisted cluster structure.

In concluding this section on structure formation from cellulose solution, Table 2.2.11 summarizes some important parameters of processing, relevant parameters of structure, and some macroscopic end-use properties of cellulose-based filaments and films.

2.2.3 Concluding remarks

Both the phenomena of limited swelling and of dissolution of cellulose comprise a more or less complete destruction of the molecular order of the native polymer by overcoming the intermolecular interactions of the macromolecules by stronger intermolecular forces or by covalent derivatization. Swelling and dissolution of cellulose are relevant for cellulose processing along two routes, i.e.
(i) the transformation of native cellulose fibers of limited length to continuous filaments or films, or to solids of special shape;
(ii) the derivatization of the polymer under homogeneous conditions resulting in a rather uniform distribution of substituents along and between the polymer chains.
The first point, i.e. cellulose structure formation from solution, is a most relevant topic of cellulose physics and could be treated only marginally in this textbook on cellulose chemistry, but will be considered briefly in connection with artificial filament spinning process from cellulose acetate, cellulose xanthogenate, and cellulose Cuam solutions. Homogeneous cellulose derivatization and its consequences on product properties will be adequately discussed in chapters 4.4 and 4.5.

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2.3 Degradation of Cellulose

Degradation of the cellulose macromolecule can be brought about with various kinds of energy input, i.e. chemical, thermal, mechanical or radiation energy (see Table 2.3.1), and it can proceed via numerous reaction routes.

Table 2.3.1. Survey of modes of cellulose degradation

Type of energy input	Mode of action
Chemical	Acid hydrolysis
	Enzymatic hydrolysis
	Alkaline degradation
	Oxidative degradation
Mechanical	Dry milling
	Wet milling and shearing
	Ultrasonic agitation
Thermal	Thermal treatment at different levels of temperature in various media
Radiation	Exposure to UV/visible radiation
	Exposure to high-energy radiation

Depending on the type of energy input and procedure, cellulose degradation can finally result in small molecules only, for example glucose, after a homogeneous acid hydrolysis, or it can come to a stop at a macromolecular level, as demonstrated by the so-called 'level-off *DP*' observed after a heterogeneous hydrolytic treatment in dilute acid. Numerous processes of cellulose degradation lead to the formation of new functional groups within the polymer moiety, and are sometimes accompanied by some crosslinking, resulting in an incomplete solubility of the degraded sample in conventional cellulose solvents. On the other hand, the rate and the course of a degradation process can be largely influenced by a previous partial or complete derivatization of the hydroxy groups of the polymer. A striking example is the strong dependence of the rate of enzymatic degradation of carboxymethylcellulose on the *DS* of the sample.

In nearly all modes of cellulose degradation, except perhaps that induced by high-energy radiation, cellulose supramolecular structure (crystallinity or fibrillar morphology) plays a decisive role in determining the rate and often also the course of a degradation process. A high supramolecular order of the polymer chain generally impedes degradation, the rate of which, however, can be remarkably enhanced by changing from a heterogeneous to a homogeneous system. This was demonstrated experimentally for acid or enzymatic hydrolysis, or

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for thermal degradation with a rate difference between homogeneous and heterogeneous enzymatic hydrolysis of glycosidic linkages being a factor of 10^3.

The most important analytical criterion for assessing quantitatively cellulose degradation is of course the change in *DP*, in combination with the change in nonuniformity of chain length distribution and chemical characterization of the sample on the macromolecular level before and after degradation. This permits a comprehensive description of a homogeneous degradation process. In the case of a heterogeneous degradation with the polymer constituting the solid phase, these data should be supplemented by information on supramolecular order and morphology and – especially in the case of fibers – results of testing mechanical properties like tensile strength.

Besides the scientific challenge of elucidation of the mechanisms of cellulose degradation, the study of these processes is of high practical relevance for understanding cellulose material properties, for the chemical processing of cellulose including functionalization, and in the chemical analysis of cellulosics. So, for example, the lifetime of cellulose-based textiles can be limited by hydrolytic or photolytic degradation. In the chemical processing of cellulose, some degradation is sometimes deliberately achieved in order to reduce solution viscosity, but more often has to be minimized in order to avoid detrimental effects on product properties. Last but not least, the instrumental analysis of cellulose derivatives by means of NMR spectroscopy or by means of chromatography frequently requires a partial or even a complete hydrolytic degradation as a necessary step in sample preparation.

This chapter on degradation of cellulose will be structured according to types of energy input. The main emphasis will be on the reaction mechanisms of degradation of cellulose itself as well as some cellulose derivatives, considering in heterogeneous degradation the molecular, the supramolecular and the morphological level, as an entity. Besides this, adequate consideration will also be given to the products of degradation and their relevance in the chemical conversion of cellulose.

2.3.1 Hydrolytic degradation of cellulose

Hydrolytic cleavage of glycosidic bonds between two anhydroglucose units is the most important route of polymer degradation in cellulose processing and analysis. Formally it can be understood as the addition of one molecule of water during cleavage of the glycosidic bond and thus as the reversal of formation of the macromolecule by polycondensation (see Fig. 2.3.1).

This cleavage of the β-1,4-glycosidic bond is catalyzed either by the H^+ ions of an acid or by the action of a cellulolytic enzyme. Both these hydrolytic processes will now be considered in some detail with regard to reaction mechanism,

rate and products formed, accentuating aspects of organic chemistry and the technology of cellulose processing.

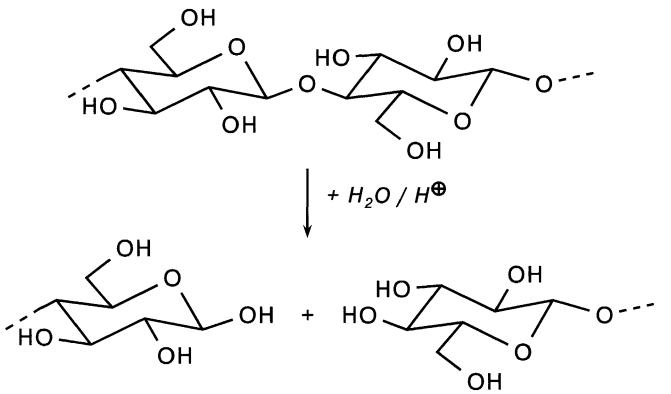

Figure 2.3.1. Principle of cellulose degradation by hydrolytic cleavage of the glycosidic linkage.

2.3.1.1 Acid hydrolysis of cellulose

Cellulose degradation by acid hydrolysis was first reported in 1855 by Calvert, just at the same time as John Mercer discovered the action of aqueous alkali on native cellulose. Both these fundamental reactions have kept cellulose chemists busy until today, the relevant publications during the different periods reflecting this development of saccharide and polymer chemistry.

According to present knowledge, the homogeneous hydrolysis of a glycoside in an acid aqueous medium is understood as a three-step process (see Fig. 2.3.2), consisting of

(i) the fast formation of a corresponding acid by addition of a proton;
(ii) the formation of a pyranosyl cation;
(iii)the addition and heterolytic cleavage of a water molecule, thus replacing finally the OR group by a hydroxy group and regenerating the H^+ ion.

As already recognized many decades ago, the acid hydrolysis of glycosidic bonds follows a first-order rate law. The rate constant k depends on the concentration of H_3O^+ ions and the temperature, as well as on the chemical environment of the glycosidic bond. With increasing acid ion concentration and temperature, the rate is increased, as expected. Whereas for cellobiose the kinetics of bond cleavage is completely characterized by just one rate constant k, for a cellotriose two rate constants are necessary for a comprehensive description, due to the different environment of the two glycosidic bonds.

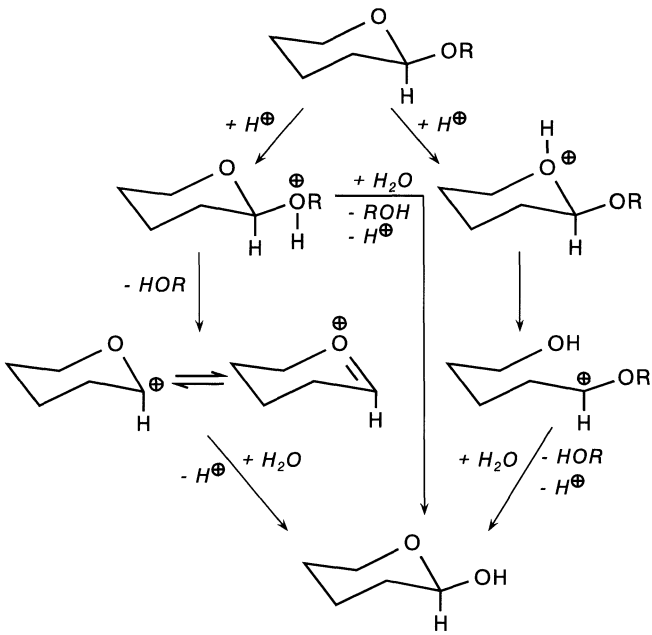

Figure 2.3.2. Mechanism of acid-catalyzed hydrolysis of a glycosidic linkage, dominant pathway via pyranosyl cation (Philipp et al., 1981a).

For practical purposes, however, a statistical bond splitting with the same probability of cleavage for any glycosidic bond can be assumed for cellulose. For a quantitative treatment of the change in *DP* during a homogeneous hydrolysis of cellulose, the 'degree of splitting' $S = 1/DP_n$ (DP_n is the number-average *DP*; Matthes, 1942) proved to be very suitable and is widely used now. According to this concept, the ultimate value of S amounts to S = 1 after cleavage of all glycosidic bonds, and the rate of bond cleavage is always proportional to the number of bonds still available for splitting, i.e. the difference between the number of bonds present at the start of hydrolysis and the number of bonds already cleaved. The first order rate law resulting herefrom can be replaced by a zero order rate law as a fisrt approximation for the initial stage of hydrolysis, arriving at a constant rate of splitting, as shown in the following scheme:

First order rate law

$$\frac{dS}{dt} = k(1-S)$$

$$\ln\left(\frac{1-S_0}{1-S_t}\right) = kt$$

Zero order rate law

$$S << 1$$

$$\frac{dS}{dt} = k$$

$$S = S_0 + kt$$

The energy of activation E_A is around an average of 131.9 ± 0.02 kJ/mol.

As a further approximation the term 1/*DP* can be substituted by the so-called fluidity, i.e. the reciprocal value of the solution viscosity of the dissolved polymer, arriving at a sufficiently linear fluidity–time plot for the initial stage of a homogeneous acid hydrolysis.

After the pioneering work of Rånby (1951) on hydrolysis of cellulose dissolved in 80–85 % phosphoric acid, numerous investigations have been reported on the kinetics and mechanisms of homogeneous acid hydrolysis, varying widely the external conditions, as well as the chemical structure of the substrate. With regard to the so-called nonuniformity, $U = M_w/M_n - 1$, as a criterion of molar mass distribution of the polymer, a decrease of this nonuniformity parameter on hydrolysis has been frequently reported after starting with a sample of rather broad molar mass distribution. A question still open to discussion is the existence of so-called weak links within the cellulose chain which are supposed to be cleaved more easily than the other glycosidic bonds even in homogeneous hydrolysis (see af Ekenstam, 1936). Also, most relevant investigations on homogeneous acid hydrolysis of cellulose are dealing with aqueous systems; a considerable decrease in *DP* or viscosity can also be observed due to hydrolytic cleavage in nearly anhydrous media. An example is shown in Fig. 2.3.3 for the decrease in solution viscosity with time of residence of cellulose trinitrite in DMF in the presence of HNO_3 and a small amount of water.

Homogeneous acid hydrolysis of cellulose derivatives has been studied predominantly with cellulose ethers due to the rather high stability of most ether groups in an aqueous acid medium. As compared with pure cellulose, the rate constant of degradation k is decisively lower for cellulose ethers in 2 M HCl at the same temperature of 30 °C, as shown by the data in Table 2.3.2.

Between these cellulose ethers, significant differences in k become visible, and a trend toward lower values of k may be concluded from these data on increasing the molar volume of the ether substituent.

Table 2.3.2. First-order rate constants k of acid hydrolysis of cellulose and cellulose ethers at 30 °C (Kasulke, 1986)

Sample	Medium	$10^5 \times k$/min	E_A (kJ/mol)
Cellulose	81 % H_3PO_4	0.41	134.0
Methylcellulose	2N HCl	0.194	132.7
Hydroxyethylcellulose	2N HCl	0.159	130.2
Carboxymethylcellulose	2N HCl	0.104	129.8

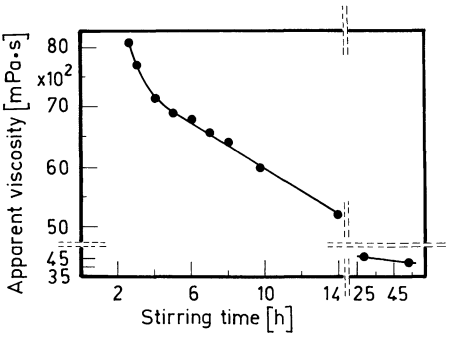

Figure 2.3.3. Viscosity of cellulose dissolved in N_2O_4/DMF versus residence time of the solution at 20 °C.

A problem situated at the borderline between homogeneous and heterogeneous acid hydrolysis and being relevant to organic and analytical cellulose chemistry is the so-called total hydrolysis of cellulose and cellulose derivatives with a maximal yield of the appropriate monomeric compounds as the decisive criterion. Required is a complete cleavage of all the glycosidic bonds on the one hand, the avoidance of a recondensation and/or a decomposition of the monomers on the other. A greater number of steps in the procedure can be suitable to minimize the first mentioned problem, while decomposition of monomers can be taken into account in optimizing the time of hydrolysis, with the monomer yield usually passing through a maximum. Todays procedures for total hydrolysis are predominantly based on 72 % H_2SO_4 or on water-free CF_3COOH as hydrolyzing agents in the initial stage, followed by stepwise dilution with water and further bond cleavage at elevated temperature. As shown by Philipp et al. (1981a), H_2SO_4 as well as CF_3COOH proved to be suitable for a high yield total hydrolysis of cellulose itself, as well as of different ethers of this polymer. With water-insoluble cellulosic compounds, H_2SO_4 showed the advantage of a higher swelling of the sample, making the glycosidic linkages more accessible to hydrolysis, while CF_3COOH permitted an easier removal of excess reagent during processing of the hydrolysate. Even carboxymethylcellulose, formally often posing problems in total hydrolysis, could be treated successfully by increasing the number of steps in the procedure with H_2SO_4 or $HClO_4$. In conclusion, it should be emphasized that all the techniques now employed for total hydrolysis of cellulose start from a heterogeneous system, which is transformed later on, via an intracrystalline swelling, into a homogeneous one, and that most of the bond cleavage takes place in this homogeneous system after dilution at elevated temperature and full accessibility of the macromolecular chains.

Quite another course of DP_n is observed in the heterogeneous hydrolysis of the cellulose fibers, i.e. in their treatment with dilute mineral acid at elevated

temperature. Although the elementary process of hydrolysis, the three-step process of protonation, bond cleavage and fragment stabilization is just the same as in homogeneous hydrolysis (see Fig. 2.3.2). The change of DP_n of cellulose in a heterogeneous acid system is characterized by a fast initial decrease, with the rate then slowing down finally to zero, and the DP_n arriving at a nearly constant value, the so-called level-off DP_n (LODP; Battista et al., 1956), as demonstrated schematically in Fig. 2.3.4.

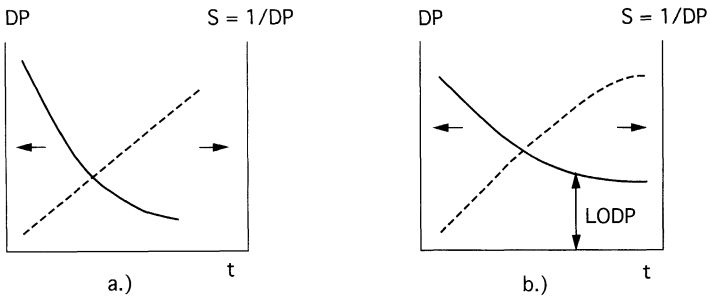

Figure 2.3.4. Course of DP_n and $S = 1/DP_n$ with time of acid hydrolysis of cellulose (schematically): (a) homogeneous; (b) heterogeneous.

On prolonged hydrolysis this LODP shows no further significant change, while the yield of hydrolysis residue decreases further. A linearization of the *DP* versus time plot can be achieved again with the degree of splitting $S = 1/DP_n$, considering only the amount of bonds to be cleaved down to the LODP, and employing a first-order rate law, or as a good approximation a zero-order rate law according to

$$1/(DP_n - \text{LODP}) - 1/(DP_n^0 - \text{LODP}) = k_0 t$$

with DP_n^0 being the original DP_n of the sample.

The LODP is primarily determined by the origin and pretreatment of the cellulose starting material, i.e. by its supramolecular and morphological structure (Table 2.3.3).

With a sample series of wood pulps differing in wood species and pulping technology, an approximately linear decrease of the LODP from about 300 to 100 with increasing content of α-cellulose (86–98 %) was observed (Steege and Philipp, 1974).

The LODP seems to be somewhat related to the size of the crystalline regions, but according to Unger et al. (1995) does not show a statistically significant correlation to the length of the cellulose crystallites. Predrying of the original sample at elevated temperature lowers the LODP to some extent, mainly due to

internal strain and microcracks in the cellulose structure, promoting glycosidic bond cleavage. The concentration of the mineral acid used in the range between 5 and 20 % HCl has a rather small bearing only on the LODP, but strongly affects the rate of hydrolysis which can be decisively increased by increasing acid concentration as well as temperature of hydrolysis. The substitution of aqueous HCl by SO_2/H_2O at elevated temperature under pressure has no significant effect on the LODP of a given cellulose sample and the same holds true for employing strong polymeric acids like polystyrene sulfonic acid in aqueous solution. Also, the rate of hydrolysis is slowed down here in the later stages due to diffusional hindrance.

Table 2.3.3. LODP of various cellulose samples

Cellulose sample	LODP
Ramie	300
Commercial wood pulps	100–300
Beech sulfite dissolving pulp	209
Beech sulfite dissolving pulp, heat treated at 140 °C	166
Cotton linters, bleached and scoured	140–180
Mercerized wood pulp	60–100
Viscose rayon (filament and staple)	25–40

A significant effect on LODP is observed by changing the medium of hydrolysis, for example by turning from water to liquids showing a higher (DMSO) or lower (propanol) swelling power to cellulose (Table 2.3.4). These observations can be understood by the counteracting effects of internal strain formation and recrystallization, with the latter being definitely favored in media of high swelling power.

Table 2.3.4. Acid hydrolysis of cotton linters (*DP* ~1600) with 1N H_2SO_4 at 80 °C in various media (Loth, 1974; Philipp and Loth, 1975)

Medium	WRV (%)	*DP*	k_0 ($DP^{-1}\ h^{-1} \times 10^3$)
DMSO	70	227	1.8
H_2O	43	166	2.8
n-Propanol/H_2O (9:1)	22	143	15.5
Methyl ethyl ketone	8	141	37.4

This clearly demonstrates the close correlations between the swelling powers of the medium of hydrolysis on one hand, the extent and rate constant of hydrolytic chain cleavage on the other.

Table 2.3.5. Effect of input of mechanical energy on acid hydrolysis of cellulose (5 % HCl, 100 °C) (Loth, 1974)

Sample	Stirring during hydrolysis	*DP* after 1 h of hydrolysis	LODP
Spruce sulfite pulp	none	181	130
DP = 750	+	170	–
Spruce sulfite pulp,	none	97	90
dry disintegrated	+	94	–
DP = 660			
Cotton linters	none	184	–
DP = 1630	+	162	–

The yield of hydrolysis residue after treatment with dilute mineral acid at a temperature of about 100 °C is generally found in the range between 90 and 95 %, depending only to a minor extent on sample pretreatment or acid concentration.

A significant effect on LODP and yield can be exerted by the input of mechanical energy before hydrolysis by milling or during hydrolysis by stirring or shearing, showing consequences on particle size and size distribution of the hydrolyzed product too. Generally this input of mechanical energy decreases particle size as well as LODP (Table 2.3.5).

From all the effects and observations outlined here briefly it can be concluded that on the basis of the fringe fibrillar model (see chapter 2.1) the course of heterogeneous acid hydrolysis can be understood by assuming a bond cleavage in the easily accessible regions of the cellulose structure only, counteracted by recrystallization of tangling chain ends and favored by microcracks and internal strain. The effects of pretreatment of the sample and of the medium of hydrolysis, as well as of input of mechanical energy on LODP fit well into this concept. It is worth mentioning that the increase in crystallinity due to hydrolysis in an aqueous medium surpasses by far the percentage calculated from the loss of amorphous materials dissolved on hydrolysis.

After a heterogeneous acid hydrolysis the cellulose fiber becomes brittle and can easily be disintegrated to a cellulose powder. This brittleness correlates well with oblique or transverse cracks visible in the morphological structure of the cellulose fibers (Dan, 1981). Particle size and particle size distribution of these cellulose powders, which are the most important criteria for end-use properties and application, can depend in a rather complex manner on the structure of the

original sample, the procedure of hydrolysis and the mechanical treatment before, during, and after the degradation process. An impression of the particle length of some types of commercial cellulose powders is given in Table 2.3.6.

Table 2.3.6. Preparation and particle length of some cellulose powders

Sample	Preparation	length (nm)
Linters powder for chromatography:	Acid hydrolysis, mechanical disintegration	
coarse		0.057
medium		0.041
fine		0.028
Pulp powder	Acid hydrolysis with input of mechanical energy	0.028
Pulp powder (for comparison)	Mechanical disintegration without hydrolysis	0.144

The data in Table 2.3.6 demonstrate the importance of the step of hydrolysis for obtaining cellulose powders of small particle size. The particle shape, however, is still not isometric and resembling somewhat the original fiber morphology. Besides particle size and size distribution, the porosity of the particles and their surface structure are of relevance in practical application, for example as tabletting aids, in dietary foods, or as chromatographic materials. The latter two criteria (porosity and surface structure) can strongly be influenced by the mode of drying the powders, as demonstrated by differences in WRV or in water vapor uptake.

Cellulose powders, especially those obtained from linters cellulose by hydrolysis with about 10 % HCl at 100 °C, down to a LODP of 150–160 and showing a particle size between 50 and 100 μm, are a convenient starting material for derivatization reactions on a laboratory scale. They still represent the polymer cellulose but already show a sufficiently low solution viscosity for convenient handling in quasi homogeneous reaction systems.

An approach to a new class of cellulosic materials was opened up by transformation of cellulose particles after heterogeneous hydrolysis to the LODP by colloidal milling to a stable gel exhibiting interesting rheological properties (Battista and Smith, 1962). The procedure of colloidal milling obviously leads to a disintegration down to the microcrystallites forming the gel network and determining its rheological properties. From experimental results obtained by ultracentrifugation and electron microscopy of these cellulose dispersions, a thickness-to-length ratio of 1 : 4 to 1 : 10 was calculated (Wulff et al., 1976). The completeness of disintegration to the microcrystallites and thus also the stability of the gels is largely influenced by the mode of drying of the hydrolyzed cellu-

lose. The stability can be enhanced by surface-active additives on the one hand, and by surface derivatization with hydrophilic groups for example by carboxymethylation on the other. Further work on the chemical and physical modification of these interesting colloidal systems can be considered a challenge to organic as well as to supramolecular chemistry of cellulose.

2.3.1.2 Enzymatic hydrolysis

Since the middle of this century enzyme-catalyzed cleavage of glycosidic bonds by cellulolytic enzyme systems has received considerable attention, promoted by the anticipation of an eco-compatible alternative choice for degrading cellulose, especially waste cellulosics, to useful products (e.g. Esterbauer and Hayn, 1985), and justified later by significant contributions to elucidation of cellulose structure as well as characterization of cellulose derivatives. Compared with acid hydrolysis, similarities as well as differences in mechanism, in response to pretreatment, and in product properties of the hydrolysis residues have to be taken into account.

Enzymatic chain cleavage takes place in dilute aqueous systems in the pH range 4–9, preferably in a buffered system at about pH 5, with a concentration of cellulosic substrate between 1 and 10 %, and the amount of enzyme protein at the 1 % level of the substrate. The principle of enzymatic degradation consists of an equilibrium reaction to an enzyme–substrate complex occurring before the rate-determining step of bond cleavage with the restitution of the enzyme:

$$E + S \rightleftharpoons E \times S \rightarrow E + P \qquad K_M = \frac{[E][S]}{[E \times S]}$$

E = enzyme
S = substrate
P = products

K_M = Michaelis-Menten-constant

The equilibrium of formation and decomposition of the intermolecular complex between enzyme protein molecules and the substrate is characterized by the dissociation constant K_M, the Michaelis–Menten constant (Haliwell and Griffin, 1973). In reality, enzymatic hydrolysis exhibits a much more complicated mechanism than acid hydrolysis. The catalyst does not consist of a well-defined, single chemical species, but is composed as a multienzyme system of numerous active proteins species, showing a synergistic effect but different action at the polymer chain, resulting in a superposition of different mechanisms of chain cleavage. The main components of a cellulolytic enzyme system are endoglucanases, cleaving the macromolecule statistically, exoglucanases (cellobiohydrolases), splitting cellobiose units from chain ends, and β-1,4-glucosidases (cellobiases), degrading cellobiose to glucose (see scheme in Fig. 2.3.5).

Each of these components has a K_M of its own, and furthermore the intermolecular enzyme–substrate complex is susceptible to displacement reactions by product molecules. Especially cellobiose leads to enzyme desorption and inhibition of further chain cleavage. The component ratio of the enzyme system differs largely between different enzyme-producing microorganisms (bacteria and fungi), and the same holds true therefore for the overall course of degradation. According to Schurz and Hönel (1989), the complicated process of enzymatic cellulose chain cleavage can at least qualitatively be modelled by dividing it into interface processes at the substrate surfaces and homogeneous steps in the liquid volume face, and by taking into account chemical reaction steps as well as diffusion processes (see also Finch and Roberts, 1985; Sprey, 1986).

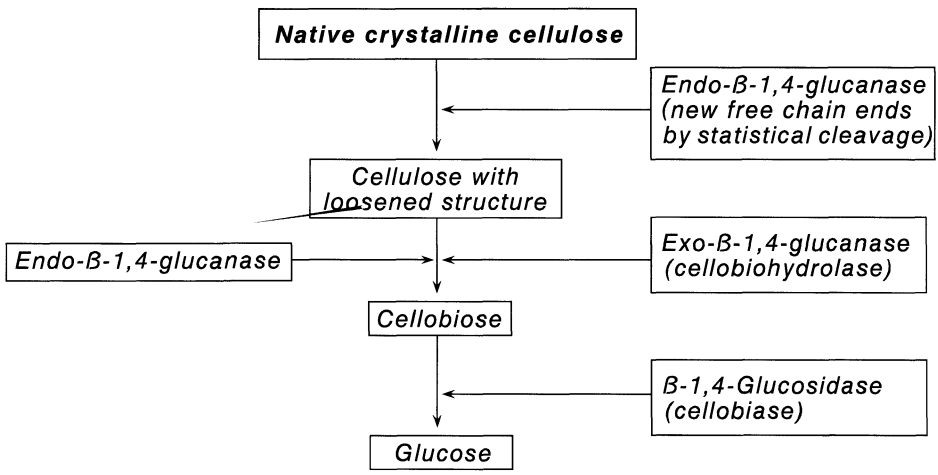

Figure 2.3.5. Scheme of enzymatic hydrolysis of cellulose.

In a homogeneous medium the enzymatic cleavage of cellulose chains can be realized only with water-soluble cellulose derivatives of low or medium *DS*. This enzymatic chain cleavage proceeds very rapidly, even at a very low enzyme protein concentration.

Under heterogeneous conditions, however, enzymatic chain cleavage is still more impeded by cellulose physical structure, i.e. by the limited accessibility of the glycosidic bonds compared with acid hydrolysis, obviously due to the large difference in size of the catalyst molecules. From results obtained in a homogeneous reaction with low substituted cellulose ethers, and extrapolated to zero *DS*, on the one hand, and experimental results with crystalline cellulose in a heterogeneous system on the other hand, a rate difference of 10^3–10^4 can be calculated for homogeneous and heterogeneous enzymatic hydrolysis of pure cellulose. The course of a heterogeneous enzymatic hydrolysis of cellulose is

usually characterized by a change of *DP* and the amount of undissolved residue, as well as the amount of reducing sugars and/or glucose formed, with the latter three criteria leading to identical results in the case of low substrate and high enzyme concentrations. Depending on enzyme system and external conditions, the residue *DP* can pass through a minimum, due to the simultaneous processes of chain cleavage and fragment dissolution, or can steadily decrease. In the case of high accessibility, the sample can at last be completely dissolved, whereas with the high *DP* and highly ordered cellulose material, a solid residue remains even after a long period of hydrolysis, indicating a partial accessibility only. While the *DP* of the sample decreases from the beginning of hydrolysis, some kind of induction period is observed with regard to the amount of residue that remains at the level of the original sample weight in the initial period of the process.

Table 2.3.7. Enzymatic hydrolysis of cotton linters by a cellulase after different pretreatments (1 % substrate, pH 4.8, 40 °C, 68 h, cellulase from $Gliocladium_{spec.}$) (Philipp et al., 1981a)

Cotton linters	Residue (%)
Untreated, *DP* = 1630	81
NH_3-treated	76
Mercerized	50
Precipitated from Cuam solution	8

As indicated by the data in Table 2.3.7, an enhanced accessibility by decrystallization with ammonia, by mercerization, or by reprecipitation from solution, leads to a decrease in hydrolysis residue under given external conditions.

The response of 'activating pretreatments', however, on the amount of residue and rate of hydrolysis, can be quite different between enzymatic hydrolysis, on the one hand, and acid hydrolysis on the other (Philipp et al., 1981a; Tables 2.3.8 and 2.3.9).

Table 2.3.8. Acid, A (7.5 % HCl, 100 °C), and enzymatic, B (1.0 % *Trichoderma cellulase*, 40 °C), hydrolysis of a beech sulfite pulp after different pretreatments (Philipp et al., 1981a)

Beech pulp	A $10^3 \times k_0$ (DP^{-1} h^{-1})	B Residue after 68 h at pH 4.7 (%)
Never dried	0.7	<1
Air dry	15	19
Wet beaten after drying	8	9
Heat treated 2 h at 140 °C after drying	22	40

While a heat treatment of the sample promotes acid hydrolysis it impedes enzymatic chain cleavage.

Table 2.3.9. Enzymatic and acid hydrolysis of cotton linters after chemical activation with different agents

Activation agent	WRV (%)	Enzymatic hydrolysis[a]			Acid hydrolysis[b]	
		R_{48} (%)	DP_{48}	$10^2 \times k_1$ (h^{-1})	R_2 (%)	LODP
Without	48	70	1210	0.6	95	172
Ammonia (liquid)	70	52	800	1.0	85	85
Hydrazine hydrate	74	36	850	–	91	116
Ethylene diamine	96	7	547	6.2	90	100
Guanidinium hydroxide (40 % aq. solution)	140	0	–	16.5	85	100

[a] 1 % substrate, 40 °C, pH = 4.8, 48 h, $Gliocladium_{spec.}$.
[b] 1 M HCl, 100 °C, 2 h.
R_{48} = residue after 48 h enzymatic hydrolysis.
DP_{48} = residue *DP* after 48 h enzymatic hydrolysis.
R_2 = residue after 2 h acid hydrolysis.

Pretreatment with nitrogen-containing basic compounds facilitates enzymatic as well as acid hydrolysis, with the order of efficiency being closely related to swelling value (WRV) of the pretreated samples. But this correlation to WRV is much more pronounced in enzymatic hydrolysis, with the guanidinium hydroxide treatment definitely taking the top position (Philipp et al., 1982a).

Summarizing the effects of cellulose supramolecular structure on the course of hydrolysis, it can be concluded that a decrease in crystalline order facilitates both enzymatic and acidic chain splitting, while enzymatic cleavage is specifically promoted by a high state of swelling of the substrate or, on the morphological level, by a high porosity and/or a high accessibility of fibrillar units (as obtained for example by wet beating). This decisive influence of the state of swelling is obviously related to the large size of the enzyme catalyst, which requires voids of at least 4–5 nm in diameter in order to pass to the site of action at the cellulose chains (Fink et al., 1992). The decrease in K_M, indicating a stronger enzyme–substrate binding on swelling the cellulose in phosphoric acid, is in line with this statement.

The residues after enzymatic treatment exhibit, in comparison with the original sample, an increase in crystallinity just as after acid hydrolysis, but in contrast with that, also an increase in WRV and an enhanced porosity (Fink et al., 1992). While the lattice type of cellulose (cellulose I or cellulose II) was found to be of minor importance only to the course of hydrolysis, it had some bearing on structural changes in the residues, which can be traced back to differences in the hydrogen bond system between these two modifications of cellulose. Regarding gross morphology, a significant fiber shortening due to transverse or oblique scission, and a broadening of fiber length distribution after enzymatic treatment of wood pulp, has been reported (Dan et al., 1983), besides an increase in fiber surface roughness and porosity.

Turning now to enzymatic hydrolysis of cellulose derivatives, it has to be stated that water-insoluble ethers and esters of high degree of substitution are not at all susceptible to enzymatic chain cleavage. The same holds true for samples neatly crosslinked by heat or radiation treatment (see later), whereas a spaced, moderate crosslinking, for example by ethylene chlorohydrin, resulting in water swellable products, can even promote enzymatic cleavage compared with the original sample. A close correlation between enzymatic degradability (characterized by the amount of sample dissolved) and the WRV, both paths of which pass through a maximum with increasing density of crosslinks, was found (Dan et al., 1980).

Enzymatic degradation of water-soluble cellulose derivatives of low to medium *DS*, can be conveniently studied via the formation of glucose and reducing splitting products and by the decrease in viscosity with time of reaction (Fig. 2.3.6).

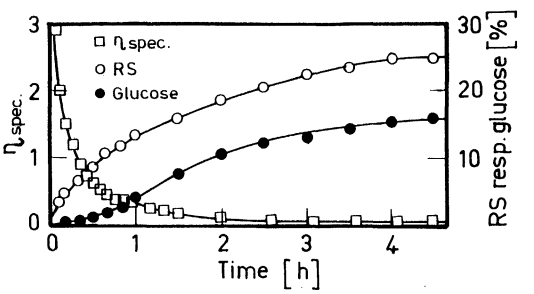

Figure 2.3.6. Course of η_{spec}, reducing splitting products (RS) and glucose formation on enzymatic treatment of a carboxyethylcellulose solution (Philipp and Stscherbina, 1992).

Due to the mechanism of enzymatic degradation discussed above, the formation of glucose lags behind that of reducing sugars, with both criteria arriving at last at a rather constant value decreasing with increasing *DS*. The change of re-

duced solution viscosity with time of reaction can be linearized within a rather wide time interval via a reduced fluidity $1/\eta_{spec.}$ versus time plot, with the zero-order rate constant k_0 decreasing steeply with increasing *DS* (Fig. 2.3.7).

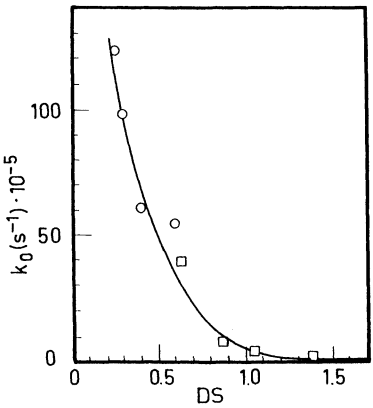

Figure 2.3.7. Zero order rate constant k_0 for the initial stage of enzymatic hydrolysis of cellulose ethers (□ carboxymethylcellulose, ○ carboxyethylcellulose) in dependence on DS (40 °C, enzyme from *Gliocladium spec.*, pH = 4.7; Kasulke, 1983).

With carboxymethylcellulose as the substrate, a significant change in solution viscosity due to enzymatic cleavage of glycosidic bonds was observed up to a *DS* of about 1.8, while formation of glucose decreased to a negligible low value already at a *DS* above 1 (Kasulke, 1986). Besides the decisive role of *DS* on the course of enzymatic degradation, the constitution of the substituent, its size and its charge obviously are also of some importance. Regarding glucose yield, methylcellulose may be an exception due to the small size of the substituent permitting a higher glucose yield (Schuseil, 1988), and with regard to drop in viscosity; a tendency toward a somewhat higher rate constant was observed with neutral cellulose ethers as compared with anionic ones of the same *DS* (Kasulke, 1986).

From the experimental evidence available today it may be concluded that sequences of three unsubstituted anhydroglucose units are a prerequisite for the sorption of protein molecules of the cellulase system to cellulose chains, i.e. for the formation of the enzyme–substrate complex (Philipp et al., 1983). This is in agreement with earlier findings (Wirick, 1968), that obviously at least unsubstituted triads are required for liberation of glucose, while a bond cleavage leading to a decrease in viscosity may occur already between the two anhydroglucose units of a diad. The increase of the dissociation constant K_M of the enzyme–substrate complex with increasing *DS*, indicating a weaker overall binding between cellulase components and cellulose chains, as well as the decrease of V_{max}, the maximal reaction rate according to the Michaelis–Menten kinetics with the *DS*, agree well with these statements.

The decisive role of the substitution pattern on the enzymatic cleavage of glycosidic bonds was demonstrated in recent studies with regioselective methylcelluloses (Kondo and Nojiri, 1994; Nojiri and Kondo, 1996). While 6-*O*-methylcellulose was degraded by a *Trichoderma cellulase* to the level of oligomers, no cleavage was observed with a sample methylated in the 2- and 3-positions.

Recent studies with isolated and purified enzyme components, especially endoglucanases, have confirmed the dominating role of *DS* in enzymatic degradability of cellulose derivatives, but indicated also a degradability of methylcellulose up to a *DS* of > 2 due to the small volume of the methyl group, which barely impedes the formation of the enzyme–substrate complex at all (Saake et al., 1997).

From a practical point of view, future application of enzymatic hydrolysis of cellulose as a tool of cellulose processing must still be considered skeptical as, in spite of the very fast elemental process of bond cleavage, the reaction volume/reaction time yield of these processes is rather low due to the limited substrate concentration and the limited temperature of reaction of about 40 °C required for securing enzyme stability. On the other hand, enzymatic hydrolysis of water-soluble cellulose derivatives has found its place in sample preparation for instrumental analysis, especially high-resolution liquid NMR spectroscopy, as a convenient way to reduce the solution viscosity without changing the pattern of functionalization. Besides this, some semiquantitative information can be obtained from the final glucose yield at a given *DS* on the uniformity of substitution along the polymer chain, as this glucose yield at a given *DS* was found to be higher in the case of a nonuniform distribution, resulting in rather long sequences of nonsubstituted anhydroglucose units.

Recent progress in the elucidation of substituent distribution along the polymer chain was achieved by combining a controlled degradation by purified endoglucanase with adequate chromatographic techniques (Saake et al., 1997).

Possible advantages of an enzyme-supported bleaching process of dissolving pulp, regarding alkali solubility, brightness and pulp viscosity control were considered recently by Christov et al. (1996) and Rahkamo et al. (1996).

2.3.2 Degradation of cellulose by aqueous alkali

Cellulose is rather stable to aqueous alkali even at a high alkaline hydroxide concentration, at and somewhat above room temperature in the absence of oxygen. A dramatic change in the supramolecular structure of cellulose occur on alkaline treatment and an addition compound, the alkali-cellulose (see chapter 4.2) is formed, from which the cellulose in the modification of cellulose II can be regenerated by neutralization. This mercerization (see chapters 2.2.1.3 and 4.2.2.2) proceeds with only a small amount of chain degradation, if the time of residence in the alkaline milieu is kept short and/or oxygen is excluded as far as possible. So, for example, in a laboratory mercerization of high-viscosity cotton

linters, an increase of splitting degree $S = 1/DP$ from 0.0006 to only 0.0007 was observed. If, on the other hand, alkali-treated cellulose fibers (lye concentration about 18 % NaOH) are kept for hours or days at or above room temperature in the presence of air, an excessive chain degradation takes place in this alkali-cellulose 'ripening' (see below).

At or above 100 °C even in the absence of oxygen, a more or less severe chain degradation takes place on treatment of cellulose with aqueous alkali hydroxide. At high alkali concentration this process results in numerous low molecular fragments, especially of carboxylic acids. At low alkali concentration, of the order of magnitude of 1 %, an endwise degradation process of the cellulose chains takes place according to the scheme shown in Fig. 2.3.8.

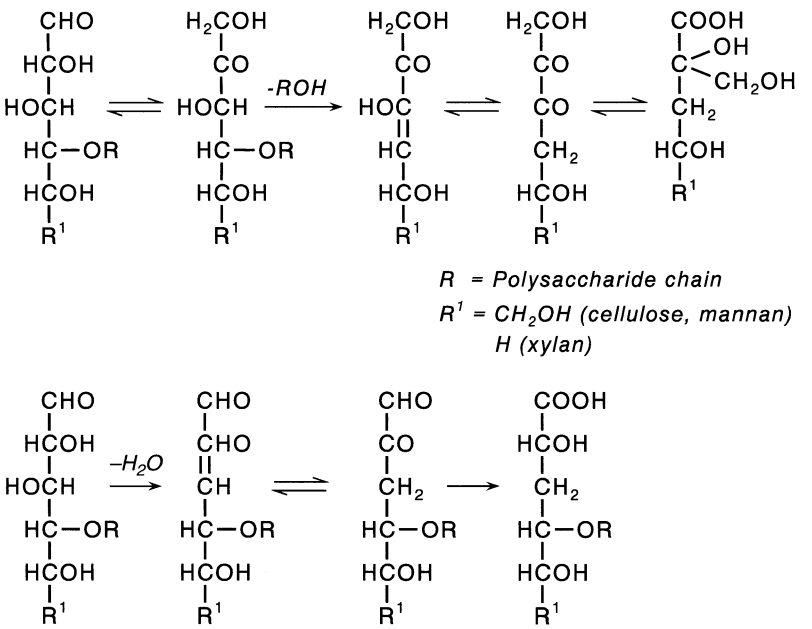

Figure 2.3.8. Scheme of endwise cellulose degradation in aqueous alkali in the absence of oxygen, including mannan and xylan (Fengel and Wegener, 1989).

At a temperature of about 100 °C, a stepwise peeling of monomer units starting from the reducing endgroups leads to a reduction in chain length. Above 150 °C the macromolecules are mainly cleaved by alkaline hydrolysis resulting in new reducing endgroups. The stepwise peeling, relevant in alkaline pulping and pulp refining, can be stopped by a competing reaction, i.e. the formation of a 3-deoxy-2-hydroxymethyl aldonic acid (see Fig. 2.3.8) as an alkali-stable end-unit. For further details the reader is referred to Fengel and Wegener (1989).

2.3.3 Oxidative degradation of cellulose

In contrast with acid hydrolysis, with its clear cut three-step mechanism of chain cleavage, oxidative degradation of cellulose can proceed via various routes comprising numerous parallel and consecutive steps of reaction. Oxidative degradation usually starts with the conversion of single anhydroglucose units to a fairly unstable derivative followed by ring opening and/or chain cleavage. Processes of oxidative degradation cover a wide range between a moderate depolymerization resulting in a macromolecular product, and a total destruction of the polymer down to CO_2 and H_2O as the final compounds. The following subchapter is centered on oxidative chain degradation, especially by atmospheric oxygen, while oxidative processes leading to well-defined macromolecular derivatives of cellulose and being accompanied by only a moderate chain degradation are briefly mentioned and will be treated in detail in chapter 4.6.

Cellulose exhibits a high stability to atmospheric oxygen under neutral and acidic conditions. Elemental oxygen at elevated temperature is now widely used in an eco-compatible bleaching of aqueous pulp suspensions buffered to the pH > 9, in order to remove residual lignin. Also, the more aggressive ozone is employed as a bleaching agent for oxidative removal of lignin at a pH of about 2.5, reducing only moderately the chain length of the cellulose molecules.

At high alkalinity, however, i.e. at pH ≥ 14, cellulose in contact with aqueous alkali is rather rapidly degraded by a complex set of autoxidation reactions already in the temperature range between 20 and 40 °C, which is started by the uptake of atmospheric oxygen. Oxygen uptake and subsequent chain degradation are accelerated by raising the temperature of reaction and also by a stronger pressing off of this steeping lye from the alkali-cellulose promoting oxygen diffusion into the fiber material. This process is practised on a large scale as the so-called 'alkali cellulose preripening' during viscose preparation by exposing an alkali-cellulose with approx. 33 % cellulose and 16 % NaOH to atmospheric oxygen. Oxygen uptake and chain degradation are further accelerated by increasing the oxygen pressure and by the presence of the cations of some transition metals like iron, manganese or cobalt. As shown by Entwhistle et al. (1949), oxygen uptake passes a maximum independence on steeping lye concentration at about 8 mol of NaOH/l.

In connection with the degradative autoxidation of alkali-cellulose, radical as well as ionic steps of the reaction have been discussed. Already about 50 years ago, Entwhistle, Cole and Wooding (Entwhistle et al., 1949) proposed, in their pioneering and still most relevant publication, a free radical chain mechanism for this autoxidation process, derived from their own experimental evidence and evaluation of the results of other groups. According to this concept, the initial rate of oxygen absorption is enhanced by the incorporation of free radical generating material into the alkali-cellulose. The catalysis of the overall process by heavy-metal ions, as well as the inhibition by organic and inorganic antioxi-

dants, is assumed to result mainly from the action of these substances in later stages of the reaction. Obviously, the positive catalytic effects are connected with an increased ratio of depolymerization to oxygen uptake, i.e. a higher utilization of the oxygen for steps of chain cleavage. For a given oxygen uptake, also the reducing group production is increased. The complexity of the reactions involved impede the formulation of a simplified reaction scheme. The effect of alkali labile sites of the chain in initial oxygen uptake and radical formation, the role of peroxides regulating the ratio of chain scission to oxidative derivatization, the effect of hydrogen atom abstraction at different sites of the anhydroglucose units, and last but not least the decisive role of free radicals and heavy-metal ions in directing the course of reaction to a more pronounced depolymerization needs to be emphasized.

Unfortunately, these promising studies of Entwhistle et al. on the elementary reactions of autoxidative alkali-cellulose degradation were not continued employing modern techniques of instrumental analysis. Later publications in this field were mainly concerned with the more practical aspect of employing this type of cellulose degradation for a deliberate and well-defined reduction of chain length and solution viscosity in the viscose process of man-made fiber spinning. In the alkali-cellulose preripening, a controlled chain degradation is achieved by exposing the disintegrated alkali-cellulose to atmospheric oxygen at a temperature between 20 and 50 °C. Of primary interest here is of course the change of *DP* depending on kind of pulp and conditions of alkali-cellulose preparation. Besides this, morphological changes connected with this alkali-cellulose ripening have been considered. As recognized rather early and studied in more detail (Bartel and Philipp, 1967), chain cleavage can be considered to proceed rather statistically and thus can be evaluated quantitatively again by applying the splitting degree concept, i.e. via a plot of $1/DP$ versus time. Experimental data fit rather well to this simple zero-order rate law in the initial stage of alkali-cellulose depolymerization, but for extending this process over a longer period of time, mostly two zero-order rate constants are necessary, a faster one for the initial and a slower one for the later stage of reaction (see Fig. 2.3.9).

The initial rate constant was found to vary widely with the type of dissolving pulp, i.e. the wood species employed and the pulping process used, while the slower rate constant in the later stage showed only rather small differences between a variety of pulps. The difference in the initial rate constants obtained from viscosimetric *DP* measurements could be traced back to differences in chain-length distribution and its change during alkali-cellulose ripening. Besides this influence of wood species and pulping technology on the course of DP_V during alkali-cellulose ripening, with its consequences on the viscosity of the viscose spinning solution, the heavy-metal ion content of the pulp and of the steeping lye, especially with regard to iron and manganese, is of great practical relevance due to the catalytic effect of these cations on autoxidative chain cleavage.

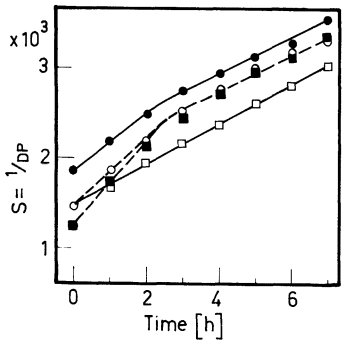

Figure 2.3.9. Course of $S = 1/DP$ versus time of aging of alkali-cellulose from different dissolving pulps (Barthel and Philipp, 1967). □ soft wood sulfate pulp, ■ beech sulfite pulp, ○ spruce sulfite pulp, ● beech sulfate pulp.

Finalizing this section on oxidative degradation by the action of atmospheric oxygen, it must be mentioned briefly that the thermal degradation of cellulose can be decisively accelerated and changed in its mechanism of reaction by the presence of oxygen at a temperature above 200 °C. Further details on thermo-oxidative degradation will be presented in a subsequent section on thermal chain cleavage of cellulose (see section 2.3.5). Just as in the case of other polymers, the action of atmospheric oxygen on cellulose and its derivatives can be inhibited by applying well-known antioxidants like benzophenone or its derivatives.

Numerous conventional oxidants like WO_3, CrO_3 and RuO_4 degrade cellulose in a rather ill-defined manner with regard to reaction mechanisms and final products. A total destruction of the polymer down to CO_2 and H_2O has long been known to occur in the system $K_2Cr_2O_7/H_2SO_4$ at elevated temperature, and is widely used for the titrimetric determination of hemicelluloses by oxidation of the polymer with a defined amount of dichromate and titration of its excess with $FeSO_4$. The effect of chain conformation on free radical depolymerization of various polysaccharides in the system Fe^{2+}/H_2O_2 was emphasized by Hjerde et al. (1994): with single-stranded polymers like alginate, hydroxypropylcellulose and carboxymethylcellulose the degree of splitting $1/DP$ shows the expected linear increase with time of reaction, while in the case of double-stranded materials, the rate of depolymerization was rather low in the initial stage due to stabilization via the supramolecular structure, and then increased steeply in the later stages of reaction.

Rather as an 'exception to the rule', the action of special oxidants on cellulose can result in fairly well-defined cellulose derivatives containing carboxylic, aldehyde or ketone groups, and exhibiting only a limited chain degradation. Examples are the formation of 6-carboxycellulose by the action of N_2O_4 or N_2O_3 (Heinze et al., 1990), or the well-known oxidation of cellulose to 2,3-

dialdehydecellulose with HIO_4, which can be subsequently transformed into carboxyl groups by oxidation with $NaClO_2$ (Nevell, 1957). These and other well-defined oxidation processes leading to cellulose derivatives will be covered in detail in the chapter on cellulose oxidation (chapter 4.6).

2.3.4 Mechanical degradation of cellulose

Input of mechanical energy into cellulose in the solid state not only leads to disintegration at the macroscopic level, but also to a destruction of the fibrillar architecture and a loss of supramolecular order. If the mechanical energy density is high enough to disrupt covalent bonds along the cellulose chains, it results in a fairly pronounced chain cleavage.

Pioneering work in this field was performed by Hess and co-workers 50 years ago, who disintegrated native cellulose in a ball mill or a vibrating ball mill, arriving at an X-ray amorphous material of low *DP* (Hess et al., 1941 and 1942). A prolonged ball milling of a normal-grade spruce sulfite dissolving pulp for about 1 week resulted in a complete loss of the crystalline X-ray peaks and a reduction of the specific solution viscosity in Cuam to less than 20 % of the original value (Philipp, 1952). Due to the large diameter of the pot of the ball mill, and an installed device for conveying the balls up to the top of the pot, the destruction of the polymer structure was performed mainly by impact of the dropping balls and not by shearing.

Besides the reduction in *DP*, the destruction of morphological and also of supramolecular structure by ball milling must be emphasized. It was concluded that the structural differences between cellulose I and cellulose II have largely but not totally vanished after excessive ball milling (Paakkari et al., 1989).

As shown by ESR spectroscopy, chain scission on ball milling proceeds by homolytic cleavage of bonds with formation of radicals and obviously not by heterolytic chain splitting. Degradation in a vibration mill leads to cleavage to chains of any length and results in an accumulation of low *DP* fragments without arriving at a LODP (Hon, 1979).

As demonstrated by the data in Table 2.3.10 (Dan, 1981), already a static pressing of linters fibers in the range between 0.5 and 5 kbar leads to a small but significant decrease in *DP*, obviously caused by cleavage of some covalent bonds along the macromolecule at points of mechanical strain concentration.

Of high practical relevance is the question of reduction in *DP* during mechanical disintegration of cellulose fibers either by dry grinding (e.g. in a cutting mill) or by wet beating (fibrillation) as required in paper making.

Some representative data on mechanical chain cleavage during dry grinding of linters and dissolving pulps are summarized in Table 2.3.11 (Schleicher and Kunze, 1995).

Table 2.3.10. Effect of pressing on the *DP* of cotton linters (Dan, 1981)

Conditions of pressing		*DP*	$S = 1/DP \times 10^3$	$10^3 \times \Delta S$ to original sample
Pressure (kbar)	Time (min)			
None		1670	0.599	0.000
0.5	15	1610	0.621	0.022
0.5	60	1580	0.633	0.034
1	15	1556	0.643	0.044
5	15	1556	0.643	0.044

Table 2.3.11. Effect of dry grinding in a cutting mill on the *DP* of cotton linters and dissolving pulp (Schleicher and Kunze, 1995)

Sample	*DP* before grinding	*DP* after grinding	$10^3 \times \Delta S$ to original sample
Cotton linters	1950	1630	0.100
Sulfite pulp (normal grade)	670	585	0.216
Sulfate pulp (prehydrolyzed)	750	670	0.160

Although linters exhibit a larger drop in *DP* than normal grade dissolving pulp, the increase in degree of splitting ΔS, indicating the number of bonds broken in the cellulose moiety, is larger for wood pulp than for linters. The increase in degree of splitting is a more sensitive criterion for evaluating the resistance of the polymer to degradation than the drop in *DP*, and leads to the conclusion that linters are finally more resistant to mechanical impact than wood pulp. During dry grinding the DP_n was found to decrease more steeply than the weight average DP_w resulting in an increased nonuniformity U of molecular weight distribution during this mechanical disintegration. The increase in carbonyl content observed after dry grinding obviously results from oxidative processes promoted by radical formation on bond cleavage. Besides the molecular level, also the supramolecular and morphological levels are strongly affected by dry milling. The decrease in X-ray crystallinity in crystallite diameter and in degree of order obtained by NMR spectroscopy is more pronounced in the case of linters than with wood pulp. Dry grinding can increase the reactivity in some processes of cellulose dissolution and in alkali-cellulose formation, but can also result in a decrease of reaction rate in systems of low swelling power, for example in acetylation with acetanhydride, obviously due to changes in the pore structure (Schleicher and Kunze, 1995).

As shown recently by CP-MAS ^{13}C NMR spectroscopy, the decrystallization of cellulose taking place in ball milling is at least partially reversible on subsequent moisturizing and drying (Wormald et al., 1996). After 1 h of milling, however, the degree of crystallinity remained considerably lower than that of the original sample after moisturizing–drying cycles. The *DP* was reduced by 40 % after 1 h milling of an acid-hydrolyzed microcrystalline cellulose powder.

Cellulose fibers suspended in liquid media are susceptible to mechanical degradation by means of an intense shearing. The drop in *DP*, however, is much less pronounced than on dry grinding or milling of the polymer. Thus, a series of cotton samples with *DP* values between 7500 and 300, obtained by acid hydrolysis of a high molecular cotton, were suspended in the nonswelling medium *n*-butanol. Cutting the samples to pieces of 4 mm in length, and then shearing in a high-speed homogenizer, only the high molecular samples with a *DP* above 3000 exhibited a decrease in chain length on shearing (Marx-Figini and Fuguni, 1995). This shear degradation leading to a 'mechanical LODP' at about 3000, and a decrease in nonuniformity of chain length distribution, is in the opinion of these authors mainly caused by destruction of so-called weak links within the macromolecules. The shearing of an aqueous suspension of cellulose fibers by beating mainly results in fibrillation, i.e. in a loss of original morphological structure and only a small decrease in *DP*. Table 2.3.12 demonstrates this for a cotton linters sample before and after different pretreatments.

Table 2.3.12. Effect of wet beating on the *DP* of cotton linters after various pretreatments (Dan, 1981)

Pretreatment	*DP* before beating	*DP* after beating	$10^3 \times \Delta S$
None	1670	1550	0.046
Decrystallization with NH_3	1580	1480	0.031
Mercerization with 18 % aqueous NaOH	1540	1380	0.076
Treatment with aqueous guanidinium hydroxide	1620	1400	0.097

The data show that shear degradation increases somewhat after pretreatment with a strongly alkaline aqueous medium. Sonication of an aqueous pulp suspension not only leads to a loosening of the morphological structure (fibrillation), but also to a small reduction in *DP* of the magnitude observed on wet beating. Sonication during alkalization of a pulp suspension promotes the interaction between sodium hydroxide and cellulose and results in a fiber shortening and an increased macropore volume within the fibers. The difference in splitting degree ΔS between a sonicated and a

nonsonicated sample increases with the alkali concentration, i.e. from 0.03×10^{-3} in 7.5 % aqueous NaOH to 0.11×10^{-3} with 18 % aqueous NaOH (Paul et al., 1986).

No systematic investigation is known concerning reduction in *DP* during shearing of homogeneous solutions of cellulose or cellulose derivatives. Some mechanical chain degradation should be taken into account with high *DP* products at a high shearing rate (Schurz, 1974).

Ultrasonic degradation has been realized with aqueous cellulose suspensions, as well as with true or colloidal solutions of cellulose derivatives, in a significant reduction in *DP* resulting in both cases.

In a study on ultrasonic degradation of cellulose nitrate samples (DP_n 400–7500) dissolved in ethylacetate at a frequency of 20 kHz, Marx-Figini (1997) emphasized the preferential degradation of long chains. The rate of degradation increased with the initial DP. Samples with a DP below 700 were not degraded at all, indicating some kind of "ultrasonic LODP". The non-uniformity parameter $U = M_w/M_n - 1$ was found to decrease significantly during the ultrasonic treatment, especially with samples of high initial DP.

2.3.5 Thermal degradation of cellulose and cellulose derivatives

Cellulose can be classified as a polymer of moderate thermal stability. It has long been known from practical use that the range of temperature of application is limited not by melting, but by a rapid chemical decomposition at temperatures between 250 and 350 °C. The complexity of thermal degradation of cellulose results from the large number of parallel and consecutive steps of reaction, from the change of the predominant reaction route with temperature of degradation, from the strong influence of the ambient atmosphere on the degradation process and, last but not least, from the important role of the structure of the cellulose sample in thermal degradation.

Some relevant data on the thermal decomposition of cellulose are summarized in Table 2.3.13.

The thermogravimetric curve of linters cellulose in dry nitrogen shows a rapid weight loss in the range between 260 and 320 °C due to formation of volatiles, leaving a carbon-rich char above 320 °C. Some of the volatiles like CO or CH_4 are inflammable in the presence of oxygen and cause the well-known burning of cellulose.

Summarizing the results of numerous groups during the recent three decades, thermal degradation of cellulose in a dry, inert atmosphere can be understood to proceed mainly by two chemical processes, i.e.

(i) splitting off of water along the cellulose chain forming 'dehydrocellulose' and leading to occasional chain scission, but maintaining in principle the β-1,4-polysaccharide skeleton

(ii) pyrolytic fragmentation leading to aromatized entities and finally most probably to a highly crosslinked carbon skeleton (Fig. 2.3.14).
The principal reaction routes including an accelerated thermohydrolytic chain cleavage in the presence of water were summarized by Baudisch (1965).

Table 2.3.13. Data on thermal decomposition of cellulose (Gröbe, 1989)

Thermal decomposition	200–270 °C
Start of thermal decomposition	
cotton linters	225 °C
wood pulps	220–240 °C
Fast endothermal degradation (N_2)	
cotton linters	~ 300 °C
wood pulp	~ 330 °C
Temperature of ignition	
cotton	390–400 °C
viscose rayon	420 °C
Maximum flame temperature	
cotton (19 % O_2)	850 °C
Heat of combustion	
cotton fabric	16.694 kJ/kg
wood pulp	14.472 kJ/kg

The first route is the prevailing one up to about 200 °C, while above 200 °C the second route gradually dominates. Figures 2.3.10–2.3.12 illustrate the complexity of thermal decomposition reactions by presenting simplified schemes (Madorsky et al., 1956; Kilzer and Broido, 1965).

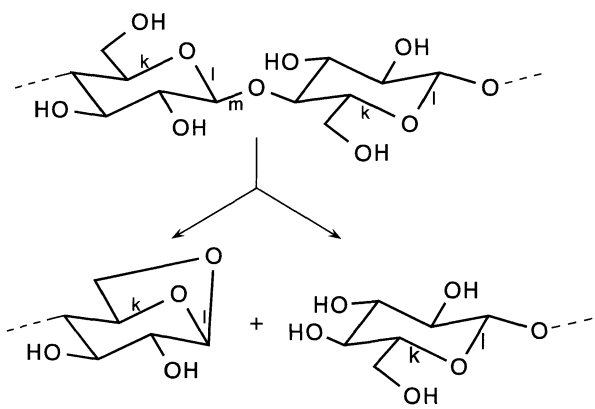

Figure 2.3.10. Scheme of thermal degradation of cellulose; cleavage of m: levoglucosan, of k, l, m: low molecular products (Madorsky et al., 1956).

A comprehensive study of cellulose char obtained by thermal degradation of microcrystalline cellulose in an inert atmosphere at temperatures between 190 and 390 °C has been performed by a combination of Curie point pyrolyses, gas chromatography, mass spectrometry, FTIR spectroscopy and solid state ^{13}C NMR spectroscopy (Pastarova et al., 1994). The abundance of aromatic building blocks (furans, alkylbenzenes and alkylnaphthalenes) increases with the temperature of degradation. It was concluded that up to about 250 °C a highly ordered β-1,4-polyglucan is principally maintained, while above this temperature a new polymer is formed, containing furanoid, hydroxyaromatic and unsaturated hydrocarbon entities, and a high number of carboxyl and carbonyl groups. With increasing temperature of degradation, further dehydration takes place, and above 320 °C disproportionation and elimination of volatiles (CO, CO_2) occurs, resulting finally in a highly condensed aromatic polymer. The whole process of thermal degradation can be decisively accelerated by the presence of oxygen on the one hand, favoring destruction of the polymer to smaller fragments, and by the presence of water vapor, especially in the region up to 200 °C, on the other, leading to hydrolytic cleavage of glycosidic bonds. The effect of the ambient atmosphere on thermal degradation with regard to the decrease of the *DP* of linters cellulose at 170 °C is described by Hess et al. (1941) and Hess et al. (1942).

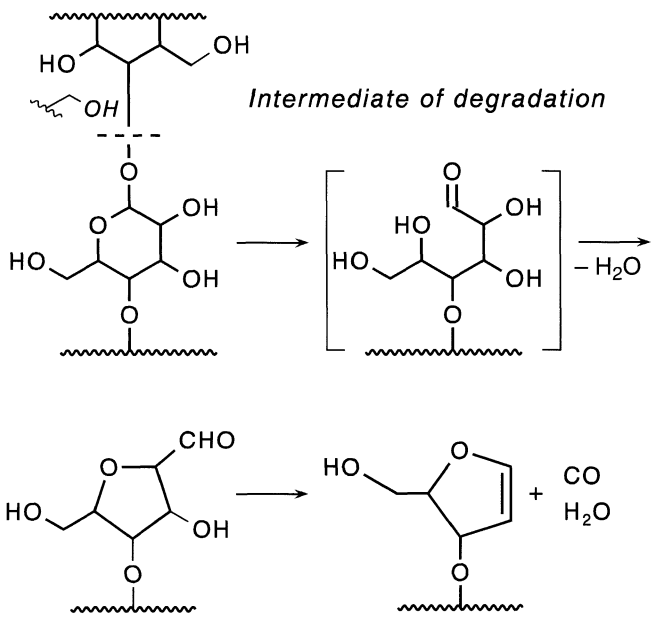

Figure 2.3.11. One of the possible reaction paths in the thermal decomposition of cellulose (Kilzer and Broido, 1965).

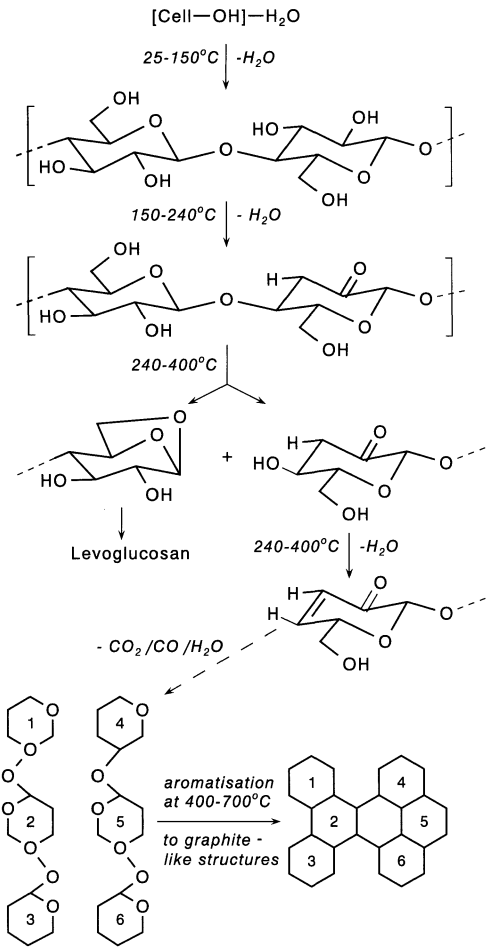

Figure 2.3.12. Thermal decomposition of cellulose to graphite-like structures (Vohler et al., 1970; Ross, 1969)

Regarding the products of degradation, levoglucosan, as well as carbonized and subsequently graphitized cellulose fibers, have found temporary interest, the former as a monomer in polymer synthesis, the latter as one of the choices for manufacturing ultra-high-strength high-modulus fibers. With respect to the mechanism of degradation, the high relevance of radical chain reactions in cellulose pyrolysis needs to be emphasized. Since the pioneering work of Kilzer and Broido (1965) and of Madorsky et al. (1956), a lot of comprehensive data has been acquired on kinetics and mechanism of thermal degradation of cellulose and its derivatives. Modern thermoanalytical techniques like thermogravimetry (TG) and differential thermal analysis (DTA) play an important part in

the determination of kinetic data at various levels of temperature, especially of parameters of activation. The Arrhenius energy of activation, however, was found to vary widely between about 120 and 260 kJ/mol of AGU, depending on the sample and conditions of degradation.

Just as for other degradation processes, it seems reasonable also for thermal decomposition to evaluate the change in *DP* via a $1/DP - t$ plot based on the splitting-degree concept. As demonstrated by the data in Table 2.3.14, the zero-order rate constant derived from this plot for the initial stage of reaction permits us to evaluate the effects of sample structure, degradation temperature or ambient atmosphere on the course of thermal degradation.

Table 2.3.14. Zero-order reaction rate of thermal and thermohydrolytic degradation (initial stage of reaction) (Data compiled from studies of Baudisch, 1965)

Degradation temperature (°C)	Medium of degradation	Reaction rate $\times 10^5$ (h^{-1})		
		Tire cord rayon	Textile rayon	Cotton linters
140	$N_2 + H_2O$	4.6	5.2	1.3
	N_2	0.1	0.3	0.3
170	$N_2 + H_2O$	27.3	30.7	8.1
	N_2	0.8	1.4	1.4
200	$N_2 + H_2O$	199	159	46
	N_2	37.5[a]	45[a]	22.5[a]

[a] Estimated from initial rate of degradation curve.

But two peculiarities of this process have to be considered here: due to the variety of chemical reactions occurring simultaneously or consecutively, a linearization is often achieved by this plot only for the initial stage of the reaction. Furthermore, thermal chain splitting is often counteracted by a thermally activated bond formation increasing the molar mass of the polymer moieties. In agreement with earlier observations (Golova et al., 1959), some kind of thermal LODP was found, which on raising the temperature of degradation from 105 to 200 °C increased from about 180 to 270 in an atmosphere of nitrogen/water vapor and a small amount of HCl. On the other hand, a significant increase in *DP* was found on heating a linters cellulose powder obtained by hydrolysis with aqueous acid down to a LODP of about 150. This enhancement of *DP* occurred in an inert atmosphere as (see Fig. 2.3.13) well as on thermohydrolytic or thermooxidative conditions, and it increased with the temperature of thermal treatment.

At a given temperature, in the range between 100 and 200 °C, the same *DP* level was finally reached by thermal degradation of the original high molecular linters, as

well as by thermal treatment of the previously hydrolyzed cellulose powder. Especially in thermohydrolysis, the determination of the *DP* was already impeded after a moderate time of thermal treatment by the formation of crosslinked gels insoluble in cuprammonium hydroxide solution (Philipp and Stöhr, 1977). Covalent bond formation and crosslinking can be assumed via acetalization with the carbonyl groups present in the degrading sample according to a mechanism proposed (Back, 1967) which is illustrated by the scheme in Fig. 2.3.14.

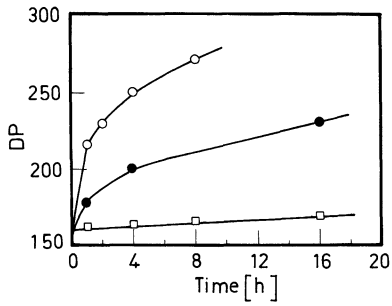

Figure 2.3.13. Increase in DP_V with time of thermal treatment of a linters cellulose powder (DP_V = 158) in a N_2 atmosphere: ○ 200 °C, ● 170 °C, □ 140 °C (Philipp and Stöhr, 1977).

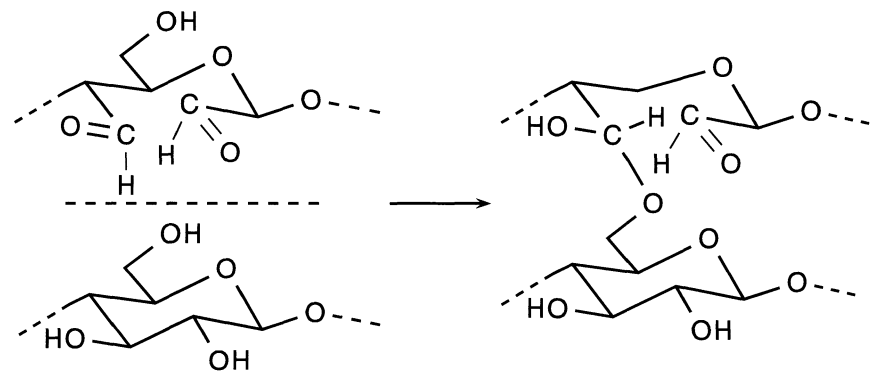

Figure 2.3.14. Scheme of the thermal crosslinking of cellulose by acetylization according to Back (1967).

Besides the molar mass of the polymer entities, also the content of carboxyl groups in the thermally degrading sample can exhibit an increase or a decrease depending on sample structure and conditions of thermal treatment. Figure 2.3.15 demonstrates the change in carboxyl group content of oxidized and non-oxidized cotton linters in a nitrogen atmosphere at 200 °C.

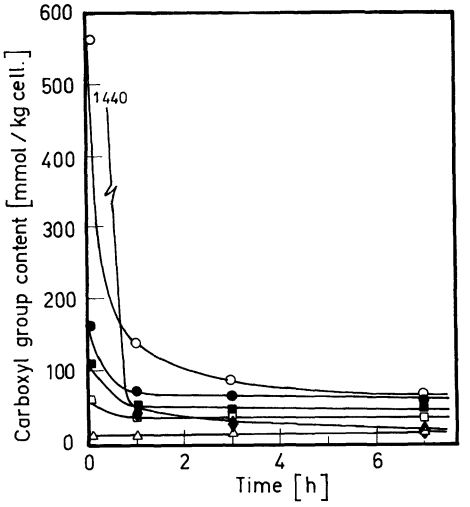

Figure 2.3.15. Change of carboxyl content of oxidized (○ 565 mmol/kg, ● 165 mmol/kg, ■ 110 mmol/kg, □ 63 mmol/kg, ◆ 1442 mmol/kg) and non-oxidized (Δ 8 mmol/kg) cotton linters with time of thermal treatment at 200 °C (Philipp et al., 1970).

From experimental evidence it can be concluded that in the range between 100 and 200 °C an initial moderate decrease in carboxyl group content is followed by a significant additional formation of these functional groups presumably promoted by disproportionation reactions, and that finally at a temperature above 250 °C fragmentation of the polymer is accompanied by a rather rapid decarboxylation. A preoxidation of the cellulose sample prior to thermal treatment results in a fast splitting off of carboxyl groups in the initial reaction stage at temperatures between 100 and 200 °C, and also in a significant acceleration of chain splitting for a periodate-chlorite-oxidized viscose rayon (van Nghi, 1970). The location of the carboxyl groups within the AGU and along the chains obviously plays an important role (van Nghi, 1970). Any route of oxidation introducing carboxyl groups leads to an accelerated thermal decomposition, while additionally formed carbonyl groups are obviously of no significant influence and even retard decomposition.

According to (Buchert et al., 1997), a high content of carboxylic groups, especially from the uronic acids present, also promotes the thermally induced yellowing of sulfate hard- and softwood pulps.

Besides the molecular level of cellulose structure so far discussed, also the supramolecular structure of the polymer is of high relevance to thermal degradation as it exhibits significant changes during thermal treatment. The degree of order determined by X-ray diffraction is retained in cotton linters as well as in textile rayon even after several hours treatment at 250 °C (Philipp et al., 1969), while the size of the ordered regions begins to decrease already at a lower degradation tem-

perature. With native cellulose samples, e.g. cotton linters, the cellulose I lattice remains unchanged even under severe conditions of thermal degradation. In the case of viscose rayon the cellulose II lattice can be gradually transformed to the high-temperature modification of cellulose IV after thermal treatment at about 200 °C. This holds true especially if this treatment is performed in glycerol, facilitating lattice transformation by swelling (Philipp et al., 1969).

The accessibility and reactivity of a cellulose sample is frequently reduced by thermal treatment in the range between 100 and 150 °C, but can also be enhanced in special cases. A decrease of the reactivity of wood pulp, for example in a subsequent acetylation, after drying at 100–150 °C is well known as hornification in the chemical processing of cellulose and is obviously mainly caused by changes in the surface structure of the polymer. The water vapor sorption of cellulose was found to decrease rather steeply after thermal and hydrothermal treatment of cotton linters or rayon at ≥150 °C (Philipp et al., 1969). On the other hand, an increase in alkali solubility of wood pulp after heating to 100–150 °C has been reported (Hernadi and Dömötör, 1981). An increase in dissolving pulp reactivity in the viscose process after a short thermal treatment at about 150 °C was concluded from the much more favorable clogging values of the viscose solution as compared with the untreated sample under the same experimental conditions (Erdmann et al., 1989). In our opinion this thermal activation in both cases is predominantly caused by microcracks in the fibrillar morphology of the fibers due to thermally induced stress, as already discussed in connection with acid hydrolysis.

The rather severe structural changes on the fibrillar level due to thermal treatment are characterized by loose fibril bundles protruding from the fiber surface, by the aforementioned microcracks and by larger fibrillar entities originating from near-surface areas, almost completely separated now from the bulk of the fiber (Philipp et al., 1981b). The effect of thermal treatment on cellulose reactivity can be understood by assuming a decrease in surface accessibility and a hydrophobicitation at the submicroscopic level on the one hand, and an increased susceptibility of fibrillar entities to subsequent processes due to partial destruction of the fibrillar architecture on the other. The net effect can be positive or negative, depending on the subsequent reaction considered.

As demonstrated by the data in Table 2.3.15, the supramolecular structure can decisively effect the rate of *DP* decrease on thermal treatment of high molecular cellulose at 100 to 200 °C. A high supramolecular order, as realized in cotton cellulose, resists thermal degradation much better than that of a sample with only moderate or low order. According to our experience, the rate of decrease of *DP* under given conditions of thermal treatment can be changed within more than one order of magnitude via the supramolecular order of the macromolecules. Its destruction by pretreatment with γ-rays lowers the temperature of fast thermal degradation and leads to increased char formation (Hanna, 1984; see chapter 2.3.6).

Table 2.3.15. Effect of cellulose source on the rate of thermal chain cleavage at 170 °C under N_2 (Hanna, 1984)

Cellulose sample	$k_0^* \times 10^5$ (h^{-1})
Cotton linters	1.4
Wood pulp	0.5–1.3
Viscose rayon staple	4
Viscose rayon (reprecipitated)	19

k_0^* = Initial zero-order rate constant from the $1/DP$ versus t plot.

An elimination of supramolecular order by dissolving the polymer prior to thermal degradation results in a much faster chain splitting in comparison with thermal cleavage of cellulose fibers at the same temperature of degradation (Table 2.3.16).

Table 2.3.16. Initial zero-order rate constants of thermal chain cleavage of cotton linters at 140 °C under homogeneous and heterogeneous conditions

Homogeneous degradation		Heterogeneous degradation	
Medium	$10^6 \times k_0^*$ (min^{-1})	Medium	$10^6 \times k_0^*$(min^{-1})
KSCN/NaSCN/DMSO	0.67	N_2	0.15
$Ca(SCN)_2 \cdot 3H_2O$[a]	18.0	$N_2 + H_2O$	0.51
NMMNO	57.0	–	–

[a] Spruce sulfite pulp.

Cellulose thermohydrolysis proceeds considerably faster in a melt of $Ca(SCN)_2 \cdot 3H_2O$ than a pure thermal degradation in a melt of NaSCN and KSCN. The rather high Arrhenius activation energy of 113 kJ/mol in homogeneous thermohydrolysis as compared with the much lower values of 60–65 kJ/mol may be due to a fixation of the water molecules in the hydration shell of the calcium rhodanite which becomes more pronounced on lowering the temperature. The remarkable high rate constant of homogeneous chain splitting in NMMNO is obviously caused by the additional oxidative action of this solvent (Chanzy et al., 1980; Lang et al., 1986).

It has to be mentioned first that according to present knowledge hemicelluloses, especially the xylans of hard wood pulp, are degraded more easily than cellulose itself. In particular, in presence of NaOH, xylans are degraded rapidly to low molecular products by "carbonyl fragmentation". With regard to the extractives present in sulfite dissolving pulps, a correlation between the content of

chlorine-containing extractives and the initial rate of decrease of *DP* on heating has been observed (Philipp et al., 1972). This acceleration is obviously due to the liberation of HCl in the early stages of degradation.

Well known to the cellulose chemist is an undesired discoloration indicating a start of degradation, sometimes observed on drying cellulose in the range of 70 to 100 °C, if the sample contains traces of e.g. sulfur or iron. A linters cellulose sample loaded with iron by soaking in a $FeSO_4$ solution was found to exhibit a much faster reduction of *DP* on heating than an untreated control sample (Horbach, 1988; Jain et al., 1987) (see Fig. 2.3.16).

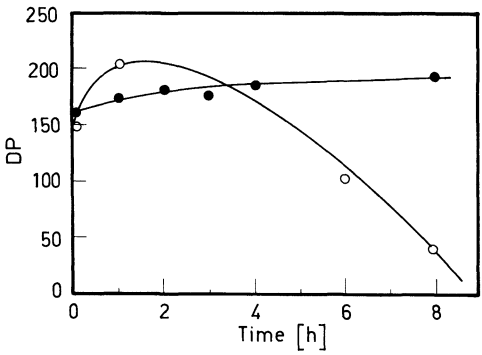

Figure 2.3.16. Change of *DP* of a LODP linters powder on thermooxidation in air at 170 °C in the original state (●) and after loading with 5 mg of Fe^{2+}/g of cellulose (○) (Philipp et al., 1981b).

The presence of various inorganic salts produces a directing action on the course of thermal degradation of cellulose by promoting C–C cleavage at the expense of C–O cleavage and increases the yield of levoglucosan. Especially $ZnCl_2$ was found to lower the temperature of rapid decomposition and to increase the formation of char and water at the expense of combustible volatiles. $ZnCl_2$ obviously catalyzes a acetalization, dehydration, and condensation of fragments, probably via a complex formed between $ZnCl_2$ and the polymer.

The thermal decomposition of numerous cellulose derivatives has been investigated by TG and DTA, arriving at data on activation energy and decomposition temperature (Horbach, 1988; Jain et al., 1987). For most of these derivatives the energy of activation for the first stage of thermal decomposition was significantly lower than that of unsubstituted cellulose (Jain et al., 1986).

In connection with the flame proofing of cellulose fibers, the effect of phosphoric acid leading to a partial phosphorylation of the polymer has found ample attention. Especially after loading partially phosphorylated samples with various transition metal cations, the production of volatiles was remarkably reduced in comparison with cellulose itself (Kaur et al., 1986). Metal complexes stable up

to 250 °C were formed and dehydration remained the prevailing reaction up to rather high temperatures. These investigations were performed by TG and DTA and evaluated the kinetic parameters, arriving at an Arrhenius activation energy of 170–240 kJ/mol, with the rate of pyrolytic weight loss as the criterion. It must be emphasized that these E_A values, obtained via the rate of weight loss, are not comparable to those of increase in degree of splitting $S = 1/DP$ mentioned earlier. For more detailed information on chemical modification of cellulose, especially by phosphorus-containing compounds with respect to flame proofing of textiles, the reader is referred to Kuryla and Papa (1973).

Studies on thermal degradation of cellulose derivatives are centered on thermoanalysis by TG and DTA and on the identification of volatiles. From the weight loss in dependence on temperature under various external conditions, the kinetic parameters of pyrolysis were determined and radical chain processes are frequently emphasized in discussing possible mechanisms of degradation (Heinze et al., 1996).

As already mentioned in connection with the accelerating effect of carboxyl groups on thermal chain splitting, a '2,3-dicarboxycellulose' (see chapter 4.6), obtained by oxidation of cellulose with $NaIO_4$ and subsequently $NaClO_2$, is particularly susceptible to thermal cleavage. But also oxidation at the C-6 position, without cleavage of the anhydroglucose ring, lowers significantly the thermal stability of the polymer, as shown by a decrease in the temperature of the start of pyrolysis with increasing content of carboxyl groups down to 100–150 °C, compared with about 250 °C for native cellulose (Ermolenko et al., 1976). Mn^{2+} cations were found to act as a catalyst (Gulko et al., 1974) and on thermooxidation of carboxy group containing celluloses, unstable peroxides were observed as intermediates (Kaputskii and Kaputskii, 1975).

The rate of thermohydrolytic chain cleavage of an aqueous CMC solution was reported to increase both with increasing *DS* and *DP* (Fimokhin, 1987).

Besides CMC, various other ethers of cellulose, i.e. methylcellulose, ethylcellulose, or sulfoethylcellulose, have been investigated by thermoanalytical techniques. On thermal decomposition of methylcellulose (Reiser et al., 1968), methanol is formed with a theoretical yield of up to a methoxy content of 25 %, and water as another main component of the volatiles is assumed to be formed by dehydration, as well as by termination of hydroxy radicals via hydrogen abstraction. Studies on thermal decomposition of ethylcellulose revealed an approx. 10 times faster degradation compared with cellulose.

Among the aliphatic carboxylic acid esters of cellulose of commercial interest cellulose acetate exhibits a better thermal stability than acetobutyrate. Thermal decomposition of cellulose acetate results in formation of CO, H_2O, acetic acid and acetylated glucose, while other esters yield rather large amounts of hydrocarbons by decomposition of the carboxylic acid moieties (Malinin et al., 1970). As effective thermostabilizers for cellulose acetate, various aromatic compounds

like hydrochinon or oligomeric benzophenone derivatives are mentioned (Fimokhin, 1987). While cellulose sulfuric acid half esters (H^+ form) are degraded by acid autohydrolysis of the glycosidic linkage already at room temperature. The Na^+ salt is moderately stable up to 130 °C, if an acid milieu is strictly avoided. In the dissolved state no significant drop in *DP* was observed after 6 h heating at 130 °C of an aqueous solution buffered with Na_2CO_3, while in an unbuffered system acidification by liberation of small amounts of H_2SO_4 leads to a self-accelerating hydrolysis of ester bonds and glycosidic linkages. Thermal stability of Na-cellulose sulfate in the solid state depends largely on its purity, especially the completeness of neutralization of the H^+ form.

The well-known thermal instability of cellulose nitrate, leading to spontaneous decomposition and even deflagration already at 100–200 °C is caused by radical cleavage of the nitric ester group according to

$$\text{Cell-O-NO}_2 \rightarrow \text{Cell-O}^{\cdot} + {}^{\cdot}\text{NO}_2$$

initiating a strongly exothermic radical chain reaction with various nitrogen oxide species acting as chain carriers, and resulting finally in the formation of H_2O, NO_x, N_2 and formaldehyde. Thermal decomposition of cellulose nitrate is promoted by residual sulfuric acid half ester groups due to incomplete 'stabilization', i.e. elimination of these groups introduced during esterification with a HNO_3/H_2SO_4 mixture. Well stabilized samples are reported to deflagrate at about 180 °C (see chapter 4.4).

Chlorodesoxycellulose, which can be considered formally as a hydrochloric acid ester of the polymer, yields rather large amounts of HCl on thermal decomposition, resulting in a pronounced dehydration and char formation at the expense of inflammable volatiles in the later stages of degradation (Ishii et al., 1978).

A thermoanalytical characterization and identification of various cellulose esters and ethers by DTA and TG was recently published in (Kaloustian et al., 1997).

2.3.6 Radiation degradation of cellulose

From tendering, i.e. a gradual deterioration of textile properties due to frequent sun-like bleaching in the moist state, it has been empirically known for many centuries that light can damage cotton or linen fabrics. Early systematic investigations in the middle of this century revealed that the quantum energy of the radiation, corresponding to its wavelength by $h\nu \sim 1/\lambda$, is the decisive criterion determining rate and mechanism of degradation resulting, e.g., in reduction of *DP*, in the formation of new functional groups, and in a decrease of tensile strength of cellulosic fibers. This section will be divided into a survey on photodegradation in the wavelength region from the far UV to the infrared, and a brief description of the effects of high-energy radiation (electron beam and γ-ray).

According to present knowledge, pure cellulose is not detectably degraded by visible or infrared light, whereas it can be damaged and changed in chemical structure via various routes by UV radiation, especially in the wavelength region below 300 nm.

In the UV region, the gas atmosphere, especially the presence of oxygen, the temperature and the presence of photosensitizing additives and/or substituents can influence the rate and course of photodegradation, besides the decisive factor of wavelength. TiO_2 added to viscose rayon as a gloss dimmer, can enhance photodamaging up to 20 % (Schurz and Windisch, 1963). A significant effect of iron or copper ions on photodegradation of cotton in the UV region is well known. A 10-fold increase in the intensity of the ESR signal due to radical formation was found after loading cotton with $FeCl_3$ and its subsequent exposure to sunlight (Hon, 1976). An accelerated photodegradation can also result from photosensitive dyes, for example antrachinon dyes, while a partial benzoylation of the polymer obviously retards photodamaging (Phillips et al., 1977). A photosensitizing effect is also exerted by the nitrate group.

Pure cellulose is not attacked by UV radiation of a wavelength larger than 300 nm, whereas in the presence of photosensitizing groups or compounds, also UV radiation in the range between 300 and 400 nm can be effective (Phillips and Arthur, 1985). According to results of various research groups, irradiation with a wavelength of 253.7 nm is particularly capable of degrading cellulose by photooxidative processes, resulting in reduction of *DP*, formation of carbonyl groups and intermediately also of peroxides (Kujirai, 1965). From model experiments (Beetik and Hamilton, 1961) with various modified cellobioses and cellopentaoses, it can be concluded that degradation in the presence of atmospheric oxygen occurs also without free carbonyl end groups and proceeds via the cleavage of the C-1–C-2 and the C-1–glycosidic-O bond. The extent of degradation was shown to increase with oxygen pressure and temperature. Obviously chain degradation proceeds preferentially in the disordered regions of the cellulose structure. In the absence of oxygen, cellulose proved to be UV-transparent above 200 nm, thus excluding photolytic interaction (Kujirai, 1965). But at shorter wavelengths, photolytic bond cleavage by 'direct primary dissociation' (Flynn et al., 1958) can take place with evolution of H_2, CO and CO_2 and a quantum yield of about 10^{-2} for H_2 and 10^{-3} for CO and CO_2. A wavelength of 185 nm was found to be especially effective, with the rate of degradation being independent of oxygen pressure and temperature. In agreement with these observations, no intermediate peroxide formation was found on irradiation at this wavelength.

Photochemical degradation of cellulose dissolved in the solvent Cadoxen (see chapter 4.3) was shown to proceed along a similar route as that observed with cellulose in the solid state.

Finally, the photodegradation of some industrially relevant cellulose derivatives will be discussed briefly on the basis of recent publications. Methylcellu-

lose can be considered as rather stable against photodegradation in a neutral or alkaline medium, while under acidic conditions UV-irradiative-induced chain cleavage takes place combined with the formation of additional C=O groups, as shown by an increase of the IR band at 1720 cm^{-1} (Yamada and Maeyama, 1989). This increase of the band at 1720 cm^{-1} was also reported by Yamada and Hirabe (1986) on UV irradiation of methylcellulose films, which besides the expected decrease in *DP* and yellowing also exhibited a change in molar mass distribution. According to Duran et al. (1990), $NaNO_2$ acts as a photosensitizer in the cleavage of methylcellulose by UV irradiation in the wavelength range 254–300 nm, forming hydroxy radicals as the active species.

Photodegradation of CMC was found to depend largely on the counterion at the anionic group. NaCMC in dilute aqueous solution exhibited an absorption maximum at 270 nm, and the rate constant of photodegradation increased with decreasing polymer concentration (Saita, 1984). Photodegradation of the Ag-salt of CMC was investigated by Miyama et al. (1993) by SERS (surface enhanced Raman spectroscopy). According to Yonezawa et al. (1992), silver in various states of aggregation can be obtained by irradiation of the Ag-salts of various carboxyl polymers, including CMC with a mercury lamp at room temperature, with the state of dispersion of the metal depending on photolysis conditions.

From numerous studies, cellulose acetate is known to be rather photostable in comparison with various other cellulose derivatives. But this stability can be significantly diminished by additives acting as photosensitizers. Margolin et al. (1994) investigated the formation of acetic acid and radicals during the photolysis of cellulose acetate, employing, additionally, 1,4-di(trichloromethyl)benzol as the photosensitizer. Identification of the various radicals formed leads to the conclusion of the formation of acetic acid by decomposition of acetoxy alkyl radicals as one of the species of the photolytic reaction chain. Shinagawa et al. (1992) confirmed the high photostability of pure cellulose triacetate, even under severe conditions. In the presence of triphenylphosphate as a plasticizer, however, considerable photodegradation of the cellulose triacetate film took place.

In contrast with numerous other substituents, the nitrate group is very liable to photochemical cleavage, and cellulose nitrate therefore has been the object of many photochemical studies and radiochemical applications (see chapter 4.4.1). A comprehensive photochemical investigation of cellulose nitrate was reported many years ago (Claesson et al., 1961). Due to a photosensitizing effect of the nitrate group, cellulose nitrate ($DS \sim 2$) dissolved in methanol proved to be susceptible to photodegradation even at a wavelength of 302 nm, with a quantum yield of 0.9×10^{-2} for the chain splitting obtained from a plot of $1/\eta$ versus dose (Claesson et al., 1961), corresponding to the quantum yield at 253.7 nm. With a wavelength of 335 nm or 364 nm respectively, no degradation was noted. In the

presence of β-naphthylamine as an additional photosensitizer, decomposition occurs also with a rather small quantum yield of 0.6×10^{-3}.

A recent study (Yamauchi et al., 1993) of the radicals involved in the photolytic cleavage of cellulose nitrate by UV radiation emphasized the formation of nitroxide-type radicals from the NO and NO_2 evolved on decomposition. Light-induced and thermally induced oxidative degradation of cellulose nitrate has been compared by Govorkov et al. (1991). Although both these processes were found to start with the cleavage of the functional group, they differed significantly with regard to products formed at a later stage of reaction. Photodegradation resulted in an accumulation of O-O-H groups, while thermodegradation led to an excessive formation of carbonyl groups. In a combined thermal and UV treatment of cellulose nitrate, the initial stage of reaction was observed to be governed by the photolytic process.

Degradation of cellulose by high-energy radiation, e.g. by γ-rays from a cobalt-60 source or by an electron beam, is characterized by a rapid decrease in *DP* due to random chain splitting, irrespective of degree of order, the formation of a large number of carbonyl groups and also of carboxyl groups, and a considerable preservation of crystallinity and fiber morphology up to high radiation doses. The primary process of bond cleavage due to ionization and excitation by a high-energy quantum is followed by energy dissipation over rather long distances and secondary radical reactions, often proceeding as a radical chain reaction and resulting in a high quantum yield (*G* value), up to 5. The decisive radiochemical processes are hydrogen abstraction leading to radical formation preferentially at the atoms C-1 and C-4, with subsequent cleavage of the glycosidic linkage and dehydration with elimination of H_2O resulting frequently in carbonyl group formation. In the presence of water, hydrogen and hydroxy radicals are formed as radiolysis products of H_2O, which participate in subsequent chain reactions, further enhancing the *G* value (Goldberg, 1989). By the same author a proportionality between radiation doses and radical concentration is reported and *G* values up to 5.5 were observed in the range of radiation dose between 10 and 20 kGy, with the radical chain reactions being terminated by recombination or disproportionation. Energy transfer along the chain over distances of up to 7 nm is concluded from degradation experiments with cellulose samples benzoylated to different degrees of substitution. As revealed by ESR experiments, radical formation occurs at low temperature (–196 °C) preferentially at C-1 and C-4, with the unpaired electrons leading to subsequent chain cleavage, while on raising the temperature up to –45 to 97 °C, dehydration and formation of allylic radicals take place. Also a β-fragmentation with radical formation at C-1 and C-4 is assumed.

The consequences of these fundamental radiochemical processes on changes of cellulose structure at the different structural levels and with regard to possible

applications will now be visualized with some examples. First of all, the rapid decrease of *DP* without arriving at a LODP, and the fast decrease of the LODP after subsequent acid hydrolysis have to be emphasized again, the latter being coursed by the susceptibility of all glycosidic bonds, even in the highly crystalline regions, to radiolytic scissions (Table 2.3.17; Philipp et al., 1982b).

Table 2.3.17. Effect of electron (e^-) and γ-irradiation on cotton linters

Radiation type	Dose (kGy)	*DP*	LODP[a]	Residue after hydrolysis (%)[a]	WRV (%)
	0	1670	158	98	41
e^-	10	520	118	95	47
	20	344	102	97	49
	40	290	70	96	50
	250	72	61	94	52
	500	60	36	85	54
	1500	39	30	64	64
γ	10	600	136	94	48
	20	420	126	95	51
	40	310	120	95	58
	250	85	67	92	57

[a] 1 M HCl, 1 h, 100 °C.

Despite the large number of chain splittings in the crystalline regions, the X-ray crystallinity was found to remain remarkably high, even after application of a high radiation dose. For example an X-ray crystallinity of 73 % is reported for a γ-irradiated cotton with a *DP* of 32, and a significant reduction in crystallinity was not observed until the radiation dose exceeded 2500 kGy. Also, the water retention value of cellulose fibers is changed only moderately by irradiation; a slight increase was observed with linters irradiated by an electron beam, while a decrease was found with electron-beam-irradiated beech sulfite pulp. While acid hydrolysis of cellulose is definitely promoted by a previous high-energy irradiation, the effect on enzymatic degradation was found to be negligible or even negative at low doses. After an almost complete breakdown of the physical structure at high dose rate, an enhancement of enzymatic degradability can be observed, and high-energy irradiation has therefore being proposed as a pretreatment of waste cellulose for feed stock application (Baker et al., 1975), or for cellulolytic degradation to glucose.

Table 2.3.18. Enzymatic degradation of preirradiated linters cellulose (linters sheets irradiated with electron-beam radiation; enzymatic degradation with culture filtrate of *Trichoderma viridae*, 68 h, pH = 5; 1 % substrate)

Radiation dose (kGy)	Residue after treatment with:	
	buffer only (%)	buffer + enzyme (%)
0	100	56
100	–	89
150	98	89
500	88	68
1500	80	32

The hindrance of enzymatic degradation after applying a low irradiation dose (see Table 2.3.18) may be attributed to some crosslinking. The G value of crosslinking of about 0.12 for beech pulp is very low as compared with that for chain splitting (Goldberg, 1989). Although the morphological structure of cellulose fibers is largely retained after irradiation, these fibers become very brittle and lose their strength and can be disintegrated by grinding or by ultrasonic treatment about 10 times faster than the nonirradiated sample.

As shown by methylation and benzylation, a partial or total derivatization of the hydroxy groups makes cellulose fibers more resistant to degradation by γ-rays obviously due to the earlier termination of the radical reaction chain. A benzylation up to a DS of 0.5 was found to be optimal for preserving a high tensile strength and a high elongation of cotton fibers after subsequent irradiation treatment.

Special consideration needs to be given to the application of high-energy radiation for pretreating dissolving pulp for preparation of viscose spinning dopes. This new process step, thoroughly investigated and technologically developed by Fischer et al. (1985), opens up a new approach to an ecological safer and economically more profitable manufacture of artificial fibers. The decisive step in the new process originally developed for beech sulfite pulp is a controlled degradation of the dissolving pulp by high-energy radiation in the dose range of 10–20 kGy down to a DP conventionally obtained after the step of alkali-cellulose preripening in the classical viscose process, thus rendering this preripening step unnecessary. The degree of splitting $S = 1/DP$ increases with the irradiation dose D according to $S_v = S_{0v} + k \cdot D^n$ $(n \neq 1)$ or $S_n = S_{0n} + k' \cdot D$, where S_v and S_n are the viscosity-based and the number-average-based splitting degrees respectively, and k, k' and n are constants. The nonuniformity parameter $U = DP_w/DP_n - 1$ decreases during the irradiation, approaching a limiting value of 1. Besides this greater uniformity of chain length distribution, the creation of

centers of disorder within the crystalline regions of the pulp during irradiation is a further benefit in the subsequent viscose preparation. The new process permits a reduction of the steeping lye concentration from about 19 to 16 % by weight and a decrease of CS_2 input of about one-third due to a more favorable distribution of the xanthogenate groups and a better CS_2 yield for the xanthation reaction proper.

2.3.7 Consequences of degradation of cellulose on its chemical processing

Besides the relevance in determining the lifetime of cellulose-based polymer materials, the degradation of cellulose along the various routes and mechanisms described here has important consequences for the chemical processing of cellulose, which will be summarized briefly.

The chain degradation of a high *DP* starting material should be avoided as far as possible in the preparation or manufacture of cellulose esters and ethers with a high solution viscosity as the decisive quality criterion. This is achieved by minimizing hydrolytic, thermohydrolytic and thermooxidative degradation, predominantly via minimizing the oxygen content in the ambient medium, by adjusting the pH and/or by minimizing the time of residence in the medium favoring degradation.

A controlled reduction of *DP* is frequently required in order to decrease solution viscosity for better processing and handling of cellulose derivatives in solution. The most important example is the step of preripening in the viscose process by an alkaline oxidative chain degradation which may in the future be substituted by a more favorable and precisely controllable high-energy radiation degradation of the dissolving pulp prior to alkalization. For facilitation of the destruction of the fiber morphology, acid hydrolysis is employed in preparing various types of cellulose powders, with the control of *DP* achieved here by the structure of the polymer itself, with the degradation being stopped after reaching the hydrolytic LODP.

Despite the comprehensive knowledge acquired today on the low molecular compounds resulting from degradation and on their mechanism of formation, the route to low molecular chemicals via cellulose degradation is not relevant today in industrial cellulose processing and must be considered as rather unlikely also for the near future. Production of glucose by acid hydrolysis practised in the first half of this century cannot compete today with the sugar-based product, and the same holds true for glucose obtained by enzymatic hydrolysis, although much effort has been put into this route during the past 25 years. And also the question is still open of whether or not an alternative pathway to ethanol by the two biotechnological steps of enzymatic cellulose hydrolysis and subsequent glucose

fermentation may be of commercial interest in the future. The manufacture of aliphatic oxycarbonic acids, failed due to problems of separation of the complex reaction mixture obtained after heat treatment in the presence of strong alkali. Levoglucosan as a product of pyrolysis has not yet found a market as a monomer in polymer synthesis. The only process practised on a large scale for several decades is the production of furfural from pentosan-rich agricultural wastes like barley husk, by a hydrothermal treatment in the presence of acid.

A rather trivial but practically important application is the caloric use of the chemical energy of lignocellulose by burning, which has received new impetus in recent years as an alternative method of energy production from a renewable source. Besides this, the centuries-old product 'charcoal', obtained by controlled pyrolysis of lignocellulose in the presence of limited amounts of oxygen, still holds its place as a specialty carbon source for several industrial processes and as an indispensable ingredient for barbecues. The production of carbon fibers on the basis of cellulose pyrolysis has not been realized today on a commercial scale as more suitable starting polymers like polyacrylonitrile fibers are available. It should be mentioned here, however, that the first carbon fibers ever produced on a commercial scale were the threads in early electrical lamps obtained by pyrolysis of cotton and later of cuprammonium rayon.

Besides its relevance to industrial chemical processing of cellulose, degradation of this polymer is of great importance in classical and instrumental cellulose analysis. In dissolving cellulose with or without derivatization for a subsequent determination of the *DP* or the chain-length distribution, chain cleavage must be avoided as far as possible of course, and the feasibility of a given procedure has to be judged by this criterion. For a controlled degradation of cellulose and its derivatives down to the level of the monomer units, an acid hydrolysis definitely is the best choice, but always has to be adapted to the type of sample for securing completeness of chain cleavage on the one hand, and avoiding side reactions on the other. Enzymatic hydrolysis can be employed with advantage for viscosity reduction of cellulose esters susceptible to acid ester cleavage. A complete destruction of the chemical structure of the polymer down to the ultimate level of CO_2 and H_2O by oxidative hydrolysis with chromic acid and sulfuric acid poses no problems with cellulose itself, but requires special procedures with cellulose derivatives. Special problems can arise in determining the degree of substitution of cellulose derivatives via the route of a complete destruction of organic matter by heating with concentrated sulfuric acid and subsequent assessment of the appropriate inorganic compound, as demonstrated by Stein (1991) for the determination of the silicon content of trialkylsilylcelluloses. Further examples will be given in chapter 3 in connection with special derivatives.

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2.4 Principles of Cellulose Reactions

Before giving a survey of the different types of cellulose reactions and describing some characteristics of syntheses with dissolved cellulose (so-called 'homogeneous reactions') and with cellulose in the solid and more or less swollen state ('heterogeneous reactions'), it seems appropriate to consider briefly some principles of chemical transformation of linear polymers as an introduction to this chapter.

2.4.1 Some principles of polymer reactions

Generally, all the reactions in organic chemistry, feasible from the viewpoint of the structural units of the monomers involved in polymer formation, can also be performed with the appropriate macromolecule. But two fundamental characteristics have to be kept in mind in realizing this principle experimentally, i.e.
(i) the limitation of the completeness of the chemical reaction and of the purity of the macromolecular reaction product caused by the covalent coupling of the repeating units along the polymer chain;
(ii) the much higher relevance of intramolecular interactions in the course of polymer reactions and on the properties of the products as compared with chemical transformations in low molecular organic chemistry.

For systematization, it is reasonable to distinguish between reactions preserving the polymer skeleton in its original shape and those changing it by crosslinking, grafting or severe degradation, although some degradation due to occasional bond cleavage between repeating units is inevitable in most polymer reactions.

As mentioned above it is also reasonable to consider separately chemical transformations starting from macromolecules dissolved and those involving solid polymers in a fairly swollen state. In the latter case, the polymer structure on the supramolecular and on the morphological level can be decisive regarding rate and extent of a chemical transformation.

We consider at first reactions of a single linear macromolecule, not affecting the polymer skeleton, i.e. so-called polymer-analogous reactions. It is demonstrated in Fig. 2.4.1 for polyvinyl alcohol that all the well-known reactions of an aliphatic hydroxy group can be performed also with the appropriate polymers.

The completeness of reactions, however, is frequently limited by the close neighbourhood of the adjacent functional groups in question. Furthermore, side reactions which are mostly unavoidable, may lead to a fairly complex structure of the reaction product. Due to the covalent linkage between the repeating units, the products of these side reactions cannot be separated by purification procedures, as practised in low molecular chemistry. The formation of even a small

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number of crosslinks – a category of side reaction observed rather frequently – can lead to gel formation in the homogeneous reaction system and impede further progress of the reaction, as for example experienced in the synthesis of polystyrene sulfonic acid by sulfonation of polystyrene. An undesired gel formation can also occur by a change in polymer solubility due to progress of conversion. Furthermore, cooperative effects can lead to a blockwise formation of reaction products, and subsequent consecutive reactions can contribute further to the complexity of the structure of the products. Besides this overall complexity, the distribution of the various functional groups along and between the chains can significantly influence product properties.

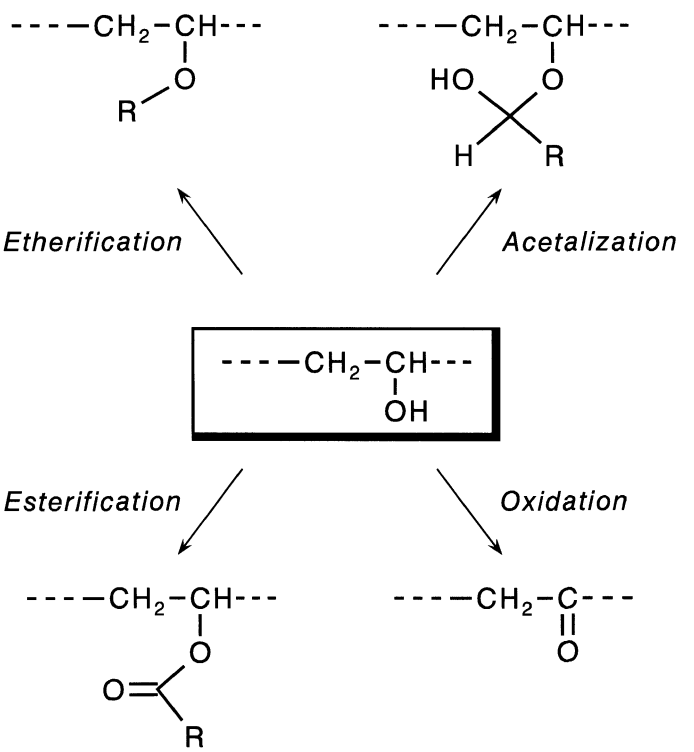


Figure 2.4.1. Sheme of typical reactions of a hydroxy group in a polymer chain.

All these points considered here in connection with polymer-analogous reactions are fairly relevant, too, in the case of chemical transformations changing the polymer skeleton. In any case, degradation of a macromolecule is by no means a reversal of its synthesis, and new and rather complex polymer structures can be formed in degradation processes as shown in the previous chapter for

thermal degradation of cellulose. The number of covalent crosslinks formed between macromolecules cannot be *a priori* concluded from the consumption of a bifunctional crosslinking agent, as usually to some extent only a monofunctional mode of reaction is realized leading to a side group but not to a crosslink (see scheme in Fig. 2.4.2).

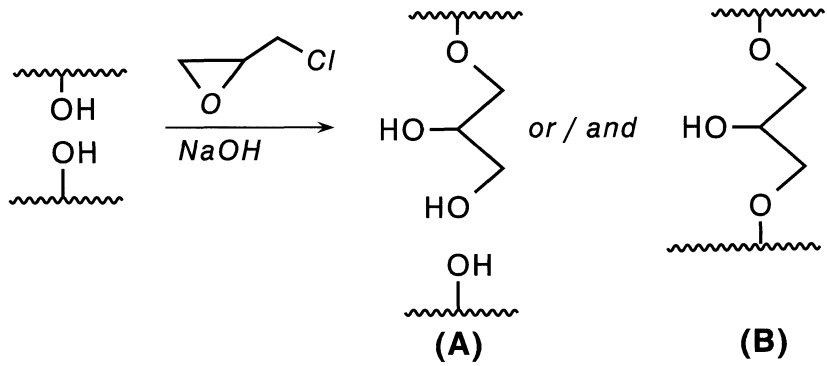


Figure 2.4.2. Mono- (A) and bifunctional (B) reaction of a crosslinking agent (epichlorohydrin) with hydroxy groups.

Grafting by addition of monomers onto active sites, being already present or being created along the macromolecule (see scheme in Fig. 2.4.3), often results in rather ill-defined polymer structures due to the variability of frequency, uniformity of distribution, length and length distribution of the grafted polymer branches in dependence on the system considered and the external conditions of the reaction. From the systematic point of view, no strict borderline exists between a polyaddition of e.g. ethylene oxide onto a hydroxy group in a polymer-analogous transformation and a graft reaction, as the number of monomers added can be varied over a wide range.

Besides the chemical transformations so far considered and based on the cleavage and formation of covalent bonds, intermolecular and coulombic interactions play an important part within the spectrum of polymer reactions. The formation of hydrogen-bond adducts with polyethylene glycol or of macromolecular charge-transfer complexes may be cited as examples from general polymer chemistry. Of considerable interest in connection with both synthetic and natural polymers is the formation of polysalts by interaction between anionic and cationic polyelectrolytes according to the scheme shown in Fig. 2.4.4. Of special relevance to the polymer chemistry of polysaccharides, is the formation of frequently ill-defined addition compounds or of fairly stable complexes between hydroxy groups of the macromolecule and various low molecular inorganic species. These interesting compounds, still posing challenging problems

with regard to their binding state, play an important role as intermediates in the organic chemistry of cellulose, and shall be treated later in detail.

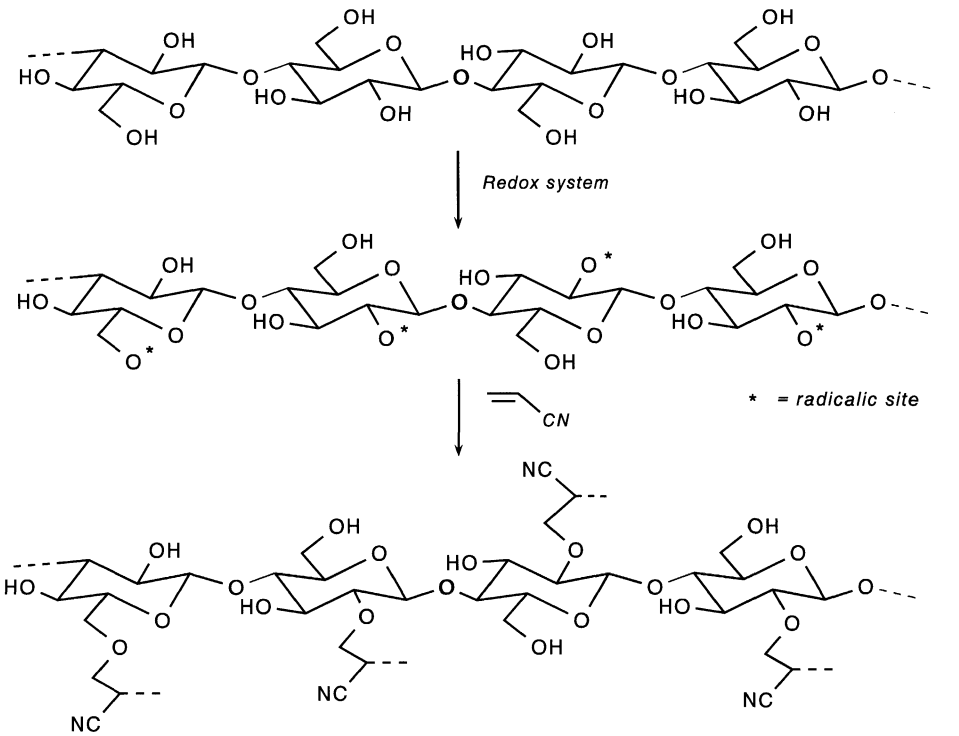


Figure 2.4.3. Scheme of cellulose grafting with acrylonitrile.

Intermolecular interaction between polymer chains generally impedes chemical transformations of the macromolecules with regard to reaction rate, and frequently also to completeness of reaction. Depending on type of reaction, reaction medium, the structure of the polymer, and external conditions, heterogeneous reactions with polymers in the solid state can proceed within a wide spectrum, from a surface-limited transformation to a quasi-homogeneous bulk reaction. The state of swelling of the polymer in the reaction medium and the molecular volume of the agent in question often play a decisive role in determining the course of these heterogeneous processes. In the case of a nonuniform ordering of the macromolecules corresponding to a two-phase model with crystalline and amorphous regions, the reaction can be limited to the latter ones or at least proceeds much faster in the disordered regions as compared with those of high order. In consequence of this general statement, frequently the reactions of cellulose can be significantly promoted by lowering the supramolecular order and/or by loosening the interfibrillar bonding

via a suitable pretreatment. On the other hand, heterogeneous chemical transformation of polymers in the solid state usually results in changes of structure at the supramolecular and morphological level with consequences for macroscopic properties including mechanical data of the polymer material.

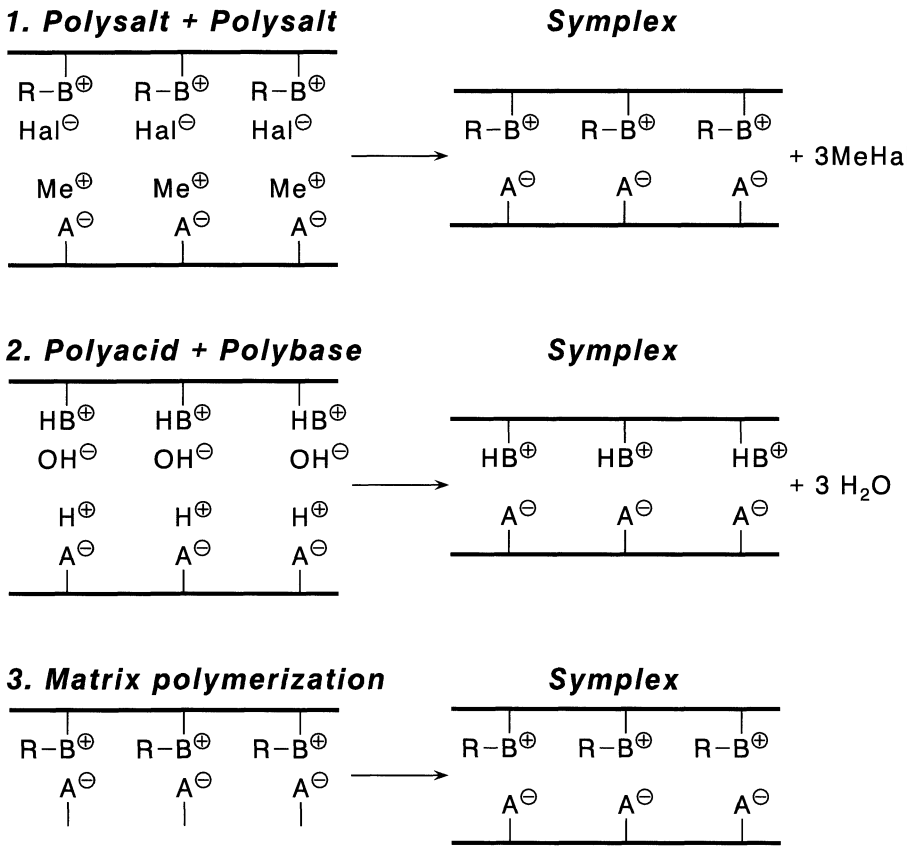


Figure 2.4.4. Routes to polysalt ('symplex') formation. (A^- acid groups like COO^-, B^+ basic groups like NR_4^+, Me metals like sodium or potassium).

Considering finally the practical relevance of polymer reactions, it must be emphasized that synthetic polymers nearly always offer a choice between monomer modification and chemical transformation of the macromolecule, with the former often being chosen. With natural polymers, on the other hand, chemical transformations of the macromolecules are the most important route to change their macroscopic properties decisively and to tailor them to special end uses. Despite the limitations and the many problems mentioned here briefly, the study of these reactions with transfer of knowledge from modern low molecular organic chemistry is

a challenge to polymer scientists and a promising route for refining and upgrading these polymer materials, continuously supplied by nature.

2.4.2 Survey of important reaction types of cellulose

The general statements presented in the previous section on polymer reactions hold true for the polymer 'cellulose', too. But two special features of this β-1,4-glucan (see Fig. 2.1.1) have to be emphasized before considering the different types of cellulose reactions in more detail, i.e.
(i) the polyfunctionality of the macromolecule resulting from the presence of free hydroxy groups within each monomer unit, which offers additional degrees of freedom for a tailored chemical transformation, but also raises additional problems with regard to uniformity of the reaction products;
(ii) the susceptibility of the glycosidic bond between adjacent AGUs to hydrolytic cleavage, which promotes chain degradation, especially in acid systems, and limits the margin of experimental procedures (e.g. in acid catalyszed esterification if products of high solution viscosity are to be obtained).

Reaction sites of practical relevance for functionalization are exclusively the three alcoholic hydroxy groups in each of the AGUs. Chemical transformations in the C-1 and C-4 regions are of interest in degradation processes and with regard to reducing end groups of the chain eventually in the chemistry of cellulose oligomers. The ring oxygen atom and that of the glycosidic linkage play some part in intermolecular interactions but not directly in covalent derivatization.

The primary hydroxy group at C-6 and the two secondary ones at C-2 and C-3 can enter into all the well-known classical reactions of an alcoholic hydroxy group, especially esterification, etherification and oxidation reactions. Besides this, they can act as ligands in metal complex formation, for example in the cuprammonium and the tartrato ferric acid complexes of cellulose (see chapter 4.3). The alcoholic hydroxy groups can form addition compounds with acids and bases, which are often fairly ill-defined, but of high practical importance for chemical cellulose processing. In the case of alkali cellulose (mostly sodium), an addition compound consisting of cellulose, sodium hydroxide and water is formed. In an extremely basic medium even a 'sodium cellulosate' can be obtained. Furthermore, alcoholic hydroxy groups show a strong tendency to form hydrogen bonds. In the case of cellulose, this tendency is the molecular basis of supramolecular ordering of the macromolecules (see chapter 2.1), but also gives rise to formation of intermolecular addition compounds with ammonia, aliphatic amines and other suitable substances.

Complete or partial esterification or etherification of the hydroxy groups are the principal reaction routes to all the cellulose derivatives available today commercially, and carrying covalently bound substituents.

Esterification is usually accomplished by reacting the polymer with the appropriate acid, its anhydride or its acid chloride as the active agent, with the high reactivity of the acid chloride preferably being employed in the case of rather weak organic acids. A special procedure is employed for the production of cellulose xanthogenate, i.e. the ester of the dithiocarbonic acid is used as the decisive intermediate in the viscose process and still the 'number one' among the cellulose derivatives with regard to annual production rate (Fig. 2.4.5).

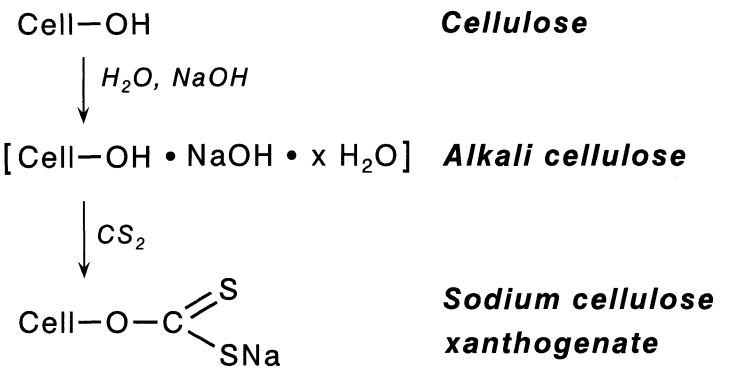


Figure 2.4.5. Scheme of cellulose xanthogenate formation.

Important cellulose esters partly produced today commercially* are (structure details see chapter 4.4):

- Cellulose acetate *
- Cellulose acetobutyrate *
- Cellulose acetophthalate *
- Cellulose xanthogenate
- Cellulose carbamate
- Cellulose formate
- Cellulose toluenesulfonate
- Cellulose nitrate *
- Cellulose sulfate *
- Cellulose phosphate *
- Halodesoxycelluloses

The principle routes to cellulose ethers, by common Williamson ether synthesis of cellulose with alkyl halides in the presence of a strong base, with alkylene oxides in a weakly basic medium, and by Michael addition of acrylic or related unsaturated compounds like acrylonitrile, are shown in the scheme in Fig. 2.4.6.

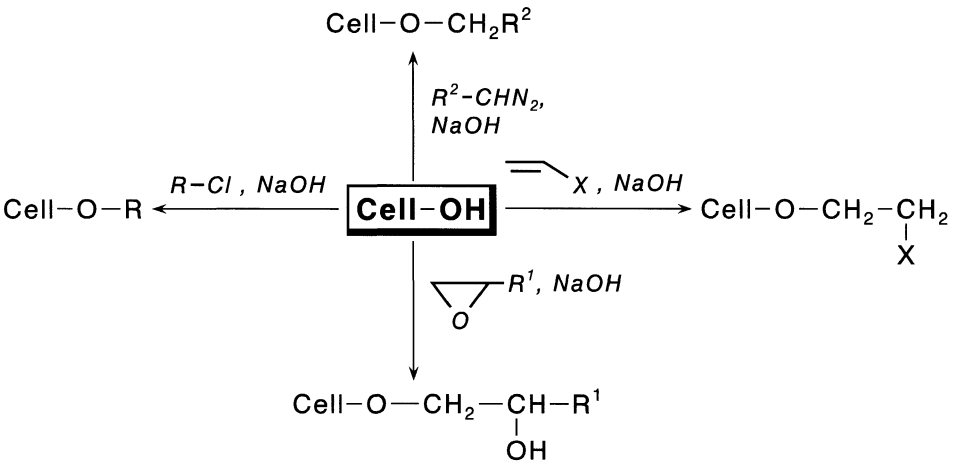


Figure 2.4.6. Routes to cellulose ethers.

Typical examples of important cellulose ethers are (structure details see chapter 4.5):

- Methylcellulose
- Ethylcellulose
- Carboxymethylcellulose
- Hydroxyethylcellulose
- Hydroxypropylcellulose
- Diethylaminoethylcellulose
- Benzylcellulose
- Alkylhydroxyalkyl mixed ethers
- Triphenylmethyl cellulose *
- Trialkylsilylcellulose *

* Not commercially manufactured.

The alkylhydroxyalkyl mixed ethers demonstrate the relevance of ethers with more than one type of ether group in todays' spectrum of cellulose derivatives.

Besides their widespread use as polymer materials or as water-soluble auxiliary products, cellulose esters and ethers frequently serve as suitable starting materials for consecutive steps of synthesis in cellulose lab-scale chemistry, as will be detailed later (volume 2) for e.g. cellulose acetate or carboxymethylcellulose. A special mention is deserved in this connection by the silyl ethers of cellulose (Fig. 2.4.7) as a versatile intermediate in laboratory synthesis of cellulose derivatives.

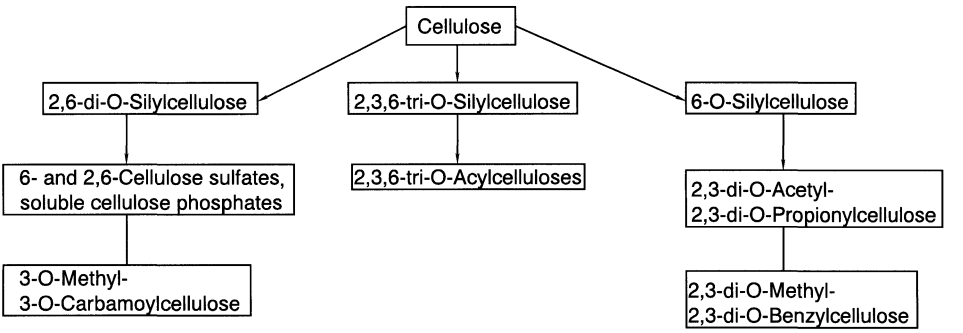


Figure 2.4.7. Trialkylsilyl ethers of cellulose as a versatile intermediate in cellulose derivative synthesis (for details see chapter 4.5.5).

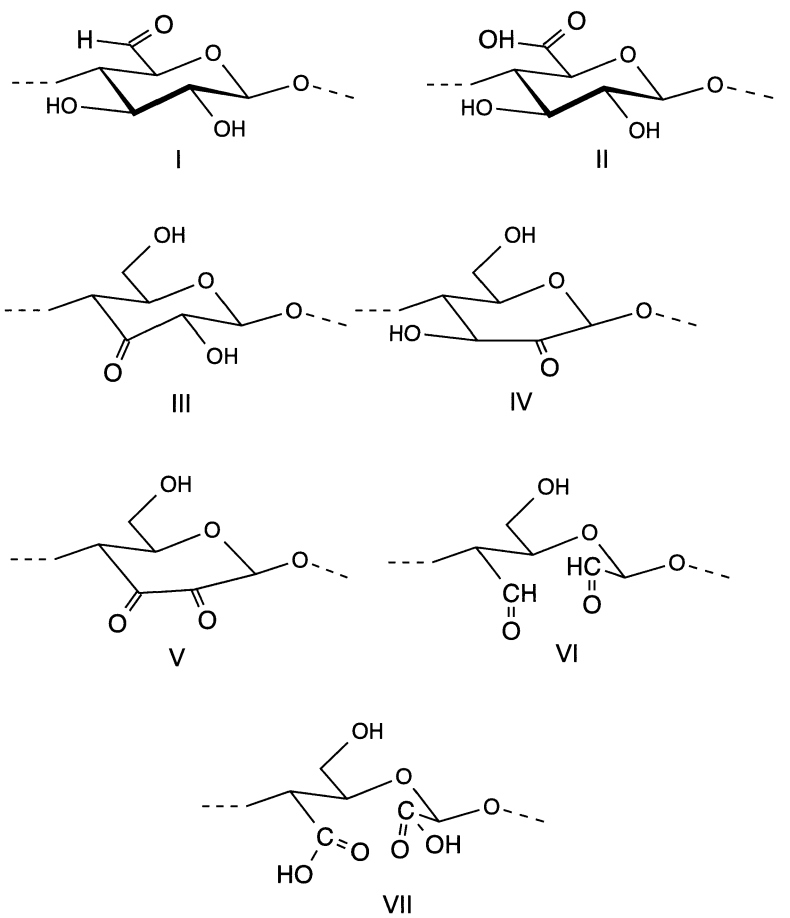


Figure 2.4.8. Products of cellulose oxidation.

According to the scheme in Fig. 2.4.8 oxidation at the hydroxy groups of cellulose can proceed in the C-6 position via an aldehyde group to a carboxyl group and in the C-2/C-3 position to keto groups or – in the case of bond scission between C-2 and C-3 – to the corresponding dialdehyde, oxidizable to the diacid, or reducible to the dialcohol. In the latter case acyclic stereoregular polymers are formed.

A first systematization of the reactions of cellulosic hydroxy groups has been elaborated by Rogowin several decades ago from the viewpoint of classical organic reaction theory (Rogowin and Galbraich, 1983). Nearly all these reactions are based on the donor reactivity of the oxygen atoms of cellulose (d^0-substrates), in relation to the synthon concept (Fuhrhop and Penzlin, 1994; Smith, 1994) with typical acceptor reagents. A special consideration is deserved in this context by halodesoxycelluloses and cellulose *p*-toluenesulfonates. These functionalized celluloses are important compounds in so far as they are excellent starting materials with acceptor reactivity for consecutive steps of synthesis altering the carbon skeleton of the polymer, either by introducing C=C double bonds, or by formation of inner anhydrides within the anhydroglucose ring. They open up a wide field of further cellulose reactions with donor reagents (H^-, R^-, NR_2, OR) and may serve as leaving groups in nucleophilic displacement reactions permitting a configurative change of the sugar residue, for example from anhydroglucose to anhydroaltrose. In the case of crosslinking and grafting mentioned above, crosslinks between cellulose chains are usually formed via ether bonds, employing bifunctional etherification agents (see also chapter 4.1). Grafting of short side chains onto the cellulose backbone sometimes occurs on etherification with alkylene oxides via addition of more than one alkylene oxide unit.

Long-chain grafting was usually accomplished by radical polymerization of vinyl compounds after creating a radical site at the cellulose chain for example by a redox reaction. As an example practised on a commercial scale some decades ago, the grafting of acrylonitrile onto viscose fiber may be cited (Rogowin, 1974). Also, block copolymers of cellulose have been prepared on a laboratory scale, by free radical polymerization onto a cellulose-based macro-initiator (Mezger and Cantow, 1983).

A complete functionalization of all the hydroxy groups of cellulose is more an exception than a rule, and most of the products manufactured on a commercial scale are partially modified cellulose compounds still containing a fairly large number of free hydroxy groups. Thus, information on the extent of reaction and on the distribution of the substituents is of great relevance in cellulose chemistry. The extent of reaction is usually characterized by the so-called degree of substitution (*DS*), denoting the average number of hydroxy groups modified per AGU, and thus covering the range from 0 to 3. Especially in connection with the viscose process, the so-called γ value is still used, which indicates the average

number of substituents per 100 AGUs, arriving at a γ value of 300 in the case of complete esterification. The cellulose xanthogenate obtained as an intermediate in the commercial viscose process often has a γ value of about 50, corresponding to a *DS* of 0.5. Industrially manufactured carboxymethylcelluloses, as the most important water-soluble cellulose ethers, usually cover a *DS* range of 0.5–1.0. Both these examples demonstrate that decisive changes in the material properties of cellulose can be realized already by chemical modification of a rather small fraction of the total number of hydroxy groups.

A partial functionalization raises the question of substituent distribution at the level of the single AGU between the positions at C-2, C-3 and C-6, along the single polymer chain, and between the macromolecules of the sample (see Fig. 2.4.9).

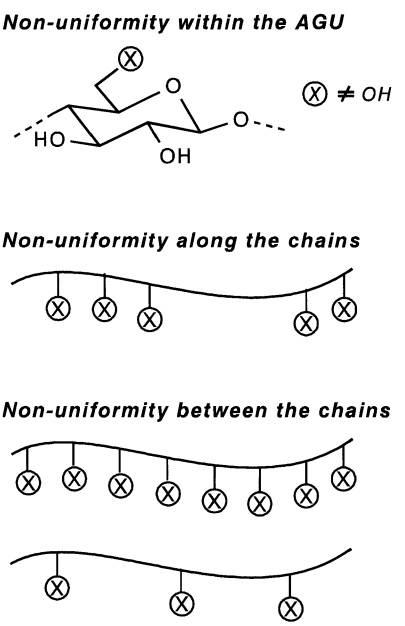


Figure 2.4.9. Functionalization patterns of cellulose products.

Distribution of functional groups within the single AGU is governed by the steric availability and the reactivity of the different hydroxy groups, with the latter often being quite different for a cellulose solution containing fairly isolated macromolecules on the one hand, and the solid polymer showing a rather high supramolecular order with the hydroxy groups engaged in hydrogen-bond formation on the other. Substituent distribution along a single chain and between the macromolecules is primarily determined by the accessibility of the hydroxy groups within a section of a single chain or along one macromolecule. The non-

uniformity of substituent distribution along and between the chains is predominantly relevant to heterogeneous reactions of cellulose, while after partial derivatization in a homogeneous system a rather uniform distribution along and between the chains can often be assumed as a first approximation.

In order to describe comprehensively the functionalization of cellulose, to understand their mechanism and kinetics and to design new routes of synthesis, it is reasonable to consider homogeneous and heterogeneous chemical transformations at the macromolecules separately in this part of the book, dealing with general principles. In a subsequent special part (Chapter 4), a subdivision according to chemical reaction types was found to be appropriate. Except the chain length degradation occurring more or less on any reaction, the chemical transformation of cellulose molecules homogeneously dissolved in an appropriate medium can be almost completely understood on the basis of today's organic chemistry. Heterogeneous derivatization, on the other hand, of cellulose in the solid usually fibrous state, must *a priori* be considered as an interdisciplinary problem of chemistry and physics of cellulose, as supramolecular order and fibrillar architecture of the specimen largely determine the extent and rate of reaction, and *vice versa* this supramolecular and morphological structure is affected by the chemical transformation. The following two subsections therefore present some general characteristics of homogeneous derivatization on the one hand, and heterogeneous cellulose reactions on the other.

2.4.2.1 Principles and characteristics of cellulose reactions under homogeneous conditions

First of all, it must be emphasized again that a full accessibility of all the macromolecules involved to a reagent during the whole course of a reaction is an indispensable prerequisite for a truly 'homogeneous' reaction of cellulose. This accessibility is neither impeded by persisting fiber fragments or gel particles from the dissolution process, nor hindered by an early gelation and phase separation of the reaction system during chemical transformation. These conditions can approximately be realized by:

(i) dissolution of cellulose in a nonderivatizing solvent, for example *N,N*-dimethylacetamide/LiCl, NMMNO or aqueous NaOH in the case of short-chain cellulose, with a subsequent derivatization reaction at the hydroxy groups;

(ii) dissolution of cellulose in a derivatizing medium, employing the primary substituent introduced during dissolution as a protecting group or as a leaving group in a subsequent reaction, for example a sulfation by transesterification of a cellulose trinitrite formed on dissolving the polymer in a N_2O_4/DMF mixture;

(iii) dissolution of a cellulose derivative in a suitable solvent, employing the substituents already present as a protecting group, leaving group or starting group for a consecutive reaction, as demonstrated for example by the acylation

of free hydroxy groups of an ethylcellulose with *DS* = 2 in a nonpolar medium (Philipp et al., 1983).

The choice between these routes depends primarily on the type of reaction and on the product in question, and also on the *DP* level of the starting material and on the *DS* desired for the product, and furthermore on possible interactions between the reagent and components of the reaction medium.

Concerning the reaction medium, the use of aqueous systems is rather more the exception than the rule due to difficulties frequently encountered in preparing homogeneous polymer solutions and due to the strong competition of the large excess of the water molecules to the comparatively few cellulosic hydroxy groups of the reagent. This point is especially relevant in acylation with acid chlorides or acid anhydrides. This holds true also for aqueous solutions of transition metal complexes of cellulose, sometimes employed formerly for homogeneous etherification. In recent work on homogeneous cellulose derivatization, dipolar aprotic liquids like DMF, DMA or DMSO, and in special cases pyridine, have been preferentially used as reaction media, the latter serving simultaneously as an adjuvant base in reactions with acyl halides. If a partially functionalized cellulose of medium to high *DS* is used as the starting material, for example an ethylcellulose of *DS* of about 2, in a subsequent acylation of the free hydroxy groups, liquids of low polarity like tetrahydrofuran or toluene can favorably act as the reaction medium. Among the nonderivatizing solvents, DMA/LiCl has proved to be suitable as a solvent for a large variety of reactions (see chapter 2.4.3).

Regarding the reactivity of the three hydroxy groups at C-2, C-3 and C-6 in homogeneous derivatization, the only general conclusion to be drawn is the statement that reaction at position 3 is strongly disfavored in comparison with positions 2 and 6, while the ranking of positions 2 and 6 depends largely on type of reaction, reagent used and reaction medium. With reagents of large molar volume, the 6-position is frequently favored due to steric reasons. The hydroxy group at C-2 is generally considered to be the most easily deprotonized, resulting in a higher intrinsic reactivity in comparison with that at C-6.

A complete functionalization up to a *DS* of 3 at a sufficiently high excess of reagent is by no means self-evident, even under homogeneous conditions. Frequently rather special procedures are required, for example in etherification with trimethylchlorosilane. Sometimes a complete substitution cannot be realized at all due to various reasons, for example steric hindrance in the case of etherification with the bulky triphenylmethyl chloride.

A partial derivatization of cellulose under homogenous conditions with the aforementioned differences in hydroxy group reactivity, raises the question of how and to what extent a preset regioselective pattern of functionalization within the AGU can be experimentally realized. Some examples of routes that were successfully pursued in recent studies are (Klemm et al., 1997):

(i) regioselective reaction at 6-OH by a bulky reagent, employing this primary substituent as a protecting or as a leaving group in subsequent steps of the reaction (e.g. silylation of cellulose with thexyldimethylchlorosilane in ammonia saturated DMF);
(ii) complete functionalization of all hydroxy groups by dissolution in a derivatizing solvent, employing regioselective reactivity of these primary substituents in a subsequent reaction, e.g. in transesterification (sulfation of a cellulose trinitrite obtained by dissolving the polymer in N_2O_4/DMF);
(iii) regioselective partial decomposition of fully modified cellulosics with the liberated hydroxy groups being used in a subsequent reaction (e.g. site-selective deacetylation of a cellulose triacetate in the 2- and the 3-positions with subsequent reesterification; Philipp et al., 1995);
(iv) competitive regioselective reaction during the transition from a heterogeneous to a homogeneous system by applying two different esterification reagents (e.g. formation of cellulose 6-sulfate by esterification with a mixture of acetic anhydride and chlorosulfonic acid in DMF and subsequent saponification of the acetate groups; Wagenknecht, 1996).

The degree of regioselectivity obtained along these routes differs widely, depending on the reaction in question and on the experimental procedure used. According to our experience the highest site selectivity within the AGU has been achieved mainly along routes (i) and (ii).

So far, homogeneous reactions of cellulose have been considered under rather ideal conditions, taking into account only the intended functionalization reaction. But in the 'lab reality' some further points are of potential relevance and can even be decisive for the success of the experiment:

First of all, the question of water content in aprotic reaction systems has to be mentioned here, which can decisively affect the course of reaction and the properties of the products. For example, a water content as low as 0.01–0.02 % is required in the cellulose/N_2O_4/DMF system in order to secure stable well-defined reaction conditions for subsequent chemical transformations of the cellulose trinitrite. The strict control of the water content, especially of the dipolar aprotic liquids employed, has to be recommended for all the work on cellulose derivatization in these systems.

Just as with other polymers, side reactions and incomplete chemical transformations can seriously impede product purity and product properties of cellulose derivatives, too. Examples encountered here rather frequently in homogenous esterification and etherification, as well as in splitting-off of primary groups, are crosslinking reactions, resulting in insoluble products, as for example observed on phosphation of cellulose, or an incomplete removal of trityl protecting groups.

Another important point is chain degradation by hydrolytic cleavage of glycosidic bonds in acidic reaction systems, as for instance observed by acid-catalyzed esterifications or by removal of protecting groups in acidic systems

(see chapter 2.3.1). This may limit the *DP* of products, e.g. in the case of regioselectively substituted carboxymethylcellulose, obtained via a tritylcarboxymethylcellulose. The minimization of the water content in dipolar aprotic solvents used as reaction media proved to be favorable also with regard to undesired chain degradation.

Even in a homogeneous system, nonuniformity in product composition can arise in very rapid reactions due to a delayed reagent distribution within the reaction volume, resulting in a partially diffusion controlled course of reaction. These effects of nonuniform reagent distribution, frequently resulting in ill-defined product properties, have to be considered especially in a scaling up of the reaction volume of high-viscosity systems with a fast reaction rate and demonstrates once more the relevance of the hydrodynamic conditions in homogeneous reaction systems of polymers. According to our experience, the disadvantages of a nonuniform reagent distribution can be counteracted even on a semi-technical scale by limiting the polymer concentration to about 2 % and/or by decreasing the reactivity of the reagent via a lowering of the reaction temperature or by partial reagent deactivation.

Colloidal phenomena, i.e. deliberate or undesired changes in the state of dispersion of the system, can play a major role with regard to product properties. A transition from a heterogeneous to a homogeneous system during the reaction, for example during dissolution of cellulose in a derivatizing solvent, generally comprises the potential disadvantages of arriving at nonuniform products of poor solubility due to persisting fiber fragments or gel particles, if the conversion is not conducted to a high degree of substitution. But, on the other hand, the combination of a heterogeneous and a homogeneous course of reaction can provide an additional degree of freedom for the procedure of synthesis, especially with regard to the regioselectivity of substitution within the AGU. The silylation of cellulose with *N*-methylpyrrolidone/NH_3/thexyldimethylsilyl chloride, e.g. which starts as a heterogeneous process and ends homogeneous, was found to yield a thexyldimethylsilylcellulose of higher regioselectivity for O-6 than the silylation of cellulose dissolved in DMA/LiCl (Klemm et al., 1995; Stein and Klemm, 1995; Koschella and Klemm, 1997).

As already mentioned, an early phase separation during a homogeneous reaction due to crosslinking by polyfunctional reagents or due to interaction between reagent and solvent components is mostly detrimental to purity and uniformity of the reaction product. On the other hand, product separation in a later stage of reaction, due to insolubility in the medium after reaching a certain level of *DS*, may be employed with advantage for product separation. As an example from our work, the synthesis of highly substituted trimethylsilylcellulose in DMA/LiCl may be cited (Schult et al., 1994), where the cellulose ether precipitated after arriving at a *DS* level of between 2 and 2.5, and could be easily separated.

Finally it must be emphasized that a homogeneous reaction may also require a tailored and often rather sophisticated procedure of product isolation and purification. From a reaction mixture containing a dipolar aprotic liquid, the polymer product can usually be precipitated by protic media like water and alcohols. The problem frequently arising here is to obtain a supramolecular structure of the precipitate suitable for further purification. Often a not too dense, flocculated and easily settling structure proved to be optimal for this purpose. Depending on the system in question, a stepwise addition of precipitant until the beginning of phase separation, prior to the precipitation process itself, an addition of electrolytes like sodium acetate, and a suitable adjustment of pH, or a combination of these means, can be recommended. The electrolytes should be easily disposable by washing. Mixtures of ethanol or acetone with water frequently proved to be adequate washing liquids for elimination of low molecular salts or organic low molecular by-products. A final careful adjustment of the pH of the product was found to be necessary, especially with ionic cellulose derivatives, before drying the product. Tailored procedures for washing, redissolving and reprecipitating the polymer reaction product have to be elaborated, if gel formation or phase separation take place already during reaction. The rather detailed considerations outlined here on isolation and purification of cellulose derivatives obtained by homogeneous reactions, are intended to accentuate the high relevance of these processes not only for a reliable product characterization, but also for product stability and for product application as cellulose specialties to be used preferentially in the biomedical field.

2.4.2.2 Principles and characteristics of cellulose reactions under heterogeneous conditions

Reactions of solids with a fairly highly ordered structure and a surrounding liquid or gaseous phase (typical heterogeneous reactions) are generally impeded with regard to rate, degree of conversion and site of conversion in comparison with an adequate chemical system with freely accessible molecules and functional groups, as realized in chemical reactions after dissolution (homogeneous reactions). This well-known fact of basic physical chemistry holds true, of course, also for the reaction of cellulose in the fibrous state. In comparison with dissolved cellulose and cellulose derivatives, the reaction rate is decreased and the degree of conversion is frequently limited, being controlled by the supramolecular order and the fibrillar architecture of the polymer.

As compared with classical examples of heterogeneous reactions, e.g. the formation of inorganic carbonates, heterogeneous reactions of cellulose show similarities, as well as differences. As demonstrated in Fig. 2.4.10, a step-shaped isotherm is observed for the binding of CO_2 to CaO in dependence on CO_2 pres-

sure, as well as in the binding of NaOH to cellulose in dependence on NaOH concentration.

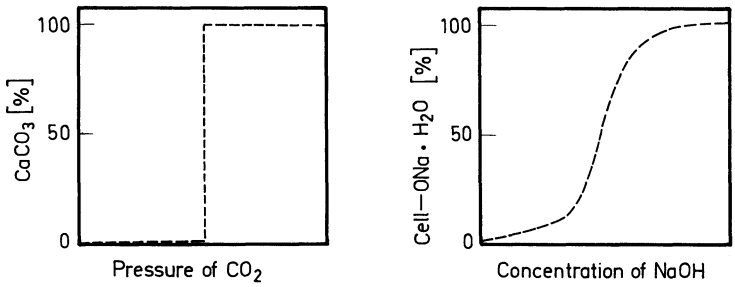


Figure 2.4.10. Reaction isotherm of heterogeneous reactions:
(a) low molecular reaction $CaO + CO_2 \rightleftharpoons CaCO_3$
(b) polymer-analogous reaction Cell–OH + $NaOH_{aqu} \rightleftharpoons$ Cell–ONa + H_2O

But the shape of the isotherm is not so clear cut and much more complicated in the transformation of the polymer due to its complex structure and the complex course of interaction between cellulose, NaOH and water. Thus for a comprehensive description and a mechanistic understanding of heterogeneous reactions of cellulose, an interdisciplinary cooperation between polymer chemistry and polymer physics is indispensable and will be duly emphasized throughout this book. After presenting some phenomenological and mechanistic highlights on heterogeneous cellulose reactions, accentuating the changes at the supramolecular entities and the fibrillar architecture, the different routes to cellulose activation, i.e. to a deliberate enhancement of the accessibility of the macromolecules, will be discussed and evaluated. Regarding cellulose structure, a two-phase model with nonuniform fringe fibrillae, based on hydrogen-bond formation as the predominant interchain interaction, is generally used (for further details see chapter 2.1).

First of all, it must be emphasized again that the effect of the cellulose structure on the course of derivatization or degradation reaction of this polymer varies within wide limits, depending on type and conditions of reaction. The spectrum observed covers the range from the so-called quasi-homogeneous reaction with a fast, usually diffusion-controlled, rate of conversion in the highly ordered and low ordered regions, to a conversion of easily available fibrillar surfaces only. Examples are nitrate formation in the system of cellulose/H_2SO_4/HNO_3, or the alkali-cellulose formation with aqueous NaOH of sufficiently high concentration, e.g. 20 %. The high degree of swelling promotes the rupture of interchain hydrogen bonds and enhances the accessibility of the macromolecules to the reagent, thus resembling somewhat the situation of a homogeneous course of reaction. This high degree of swelling, resulting in a gel-like system, can, how-

ever, diminish the rate of a consecutive reaction due to diffusional hindrance, as shown earlier for the xanthation of a very highly swollen alkali cellulose (Philipp, 1956), or more recently for ethylcellulose formation by reaction of alkali cellulose with ethyl chloride (Misina and Sarkov, 1970). As an example at the other end of the spectrum, acetylation of native cellulose under mild conditions may be mentioned here with the reaction coming to a stop after transformation of a thin surface layer.

Numerous reactions are situated between these two borderline cases. In carboxymethylation of alkali cellulose the ratio of reaction rates of homogeneous to heterogeneous reaction, is only about 4, due to the high state of swelling even of the highly ordered regions (Dautzenberg and Philipp, 1979). These ratio, however, can be orders of magnitude higher in the case of glycosidic bond cleavage under conditions of minimal swelling (see chapter 2.3; Philipp et al., 1981).

Frequently the rate and/or the ultimate degree of conversion of the low ordered regions is observed to be much higher than that of the highly ordered (crystalline) ones. Quite a lot of so-called 'chemical methods for accessibility determination' have been published based on this principle. Well-known are deuterium exchange, i.e. the substitution of hydrogen atoms in cellulosic hydroxy groups by deuterium atoms from ambient D_2O (Mann and Marrinan, 1956), and the ethanolysis of glycosidic bonds in regions of low order (Sarkov and Levanova, 1959; Sarkov, 1961). Both methods result in a subdivision of the total structure into an accessible and an inaccessible part. Other techniques, like the oxidation by NO_2 in CCl_4, or an esterification with formic acid, employ a stepwise intensification of one of the reaction parameters like reagent concentration or temperature in order to arrive at a so-called lateral order spectrum (Marchessault and Howsmon, 1957; see also chapter 2.1). The relevance of these methods for practically evaluating the reactivity in the chemical processing of cellulose is at least questionable, as the results obtained by the various methods often differ rather widely, and frequently cannot be correlated closely enough to the performance of cellulose samples in technical processes of derivatization.

As already indicated by the role of swelling, the course and mechanism of heterogeneous reactions of cellulose is determined by a mutual interaction between supramolecular structure and chemical transformations, with the rate of reagent penetration and the splitting of hydrogen bonds by the driving force of the reaction being the decisive parameters. This mutual interaction generally comprises the molecular structure with regard to chain conformation, the supramolecular one with regard to lateral order and the morphological one with regard to fibrillar architecture. Depending on the system considered, the fibrous morphology of the starting material can either be retained throughout the reaction, or a transition to a homogeneous system due to unlimited swelling, i.e. dissolution of the polymer, can occur at a later stage of the process. The latter case, realized for example in dissolution acetylation of cellulose, or in an emul-

sion xanthation of cellulose in a dispersion of CS_2 in aqueous NaOH, has been considered already in the previous subsection and in connection with cellulose solvents and their mechanism of action (see chapter 2.2). Also, the two borderline cases that are conceivable for the course of dissolution, i.e. a peeling off process, due to a rather slow surface reaction with subsequent fast dissolution of the converted chain molecules and a dissolution via special swelling structures. It is reasonable, therefore, to center subsequently on the structural changes connected with heterogeneous derivatization of cellulose, retaining a solid state structure resembling at least somewhat the fiber structure of the starting material.

On the macromolecular level, a nonuniform density of functionalization along the single chain and between chains has *a priori* to be taken into account. Its extent depends on the difference in accessibility between the highly ordered and the rather amorphous regions in the polymer structure. For the xanthation of alkali cellulose, this nonuniform density of substitution is favored by a large, high molecular fraction of the alkali cellulose (Fischer et al., 1996). For other cellulose derivatives of technical relevance, information on substituent distribution along and between the chains in dependence on starting material and conditions of the reaction is still rather scarce. Regarding the functionalization pattern within the single AGU, the 3-position is generally not favored in heterogeneous reactions also. In comparison with a homogeneous course of reaction, a somewhat stronger preference for the 2- as compared with 6-position can be stated, caused perhaps by the very strong engagement of the C-6 hydroxy group in hydrogen-bond formation. As examples for this '2 preference' the fiber xanthation and the carboxymethylation of alkali cellulose can be cited. Also for crosslinking of cellulose with epichlorohydrin in aqueous NaOH, a reactivity ranking of the hydroxy groups in the order C-3 < C-6 < C-2 has been reported (Fanter, 1980).

At the supramolecular level, a higher degree of conversion can be expected in the amorphous regions as compared with the crystalline entities, at least at the beginning of the reaction and/or under rather mild reaction conditions (low reagent concentration). It has been observed experimentally, e.g. for the binding of NaOH to cellulose in dependence on NaOH concentration in an aqueous medium. Progress of the reaction within the highly ordered regions after surpassing the accessibility barrier by intensification of the reaction conditions, is frequently indicated by the appearance of a new X-ray pattern corresponding to a change in lattice dimensions without loss of the crystalline order. The degree of order, however, can be diminished due to an excessive swelling in connection with reagent penetration into the lattice. Lattice dimensions often are enlarged in comparison with those of the original polymer. With cellulose I as the starting material, the reaction sometimes takes place rather selectively in one lattice plane as a so-called lattice layer reaction, with the corresponding lattice spacing

increasing with the degree of substitution. Fiber xanthation of alkali cellulose, as one of the most comprehensively investigated heterogeneous derivatization reactions, can be mentioned here as an example (Hess et al., 1951). As a consequence of the other crystalline lattice, these layer reactions cannot proceed in the same way with cellulose II, and the reactivity ranking of both these modifications obviously depends on the reaction in question. Possible correlations between the reactivity of crystalline regions of cellulose and corresponding changes in hydrogen-bond structure of cellulose I and cellulose II were recently studied (e.g. Kamide and Masatoshi, 1994).

Besides the percentage, size, and perfectness of the crystalline regions, the fibrillar architecture of the cellulose fiber has a strong bearing on the course of heterogeneous reactions, especially on the uniformity of substitution and the product solubility. It has been known on an empirical basis for a long time in the technical processing of dissolving pulps, that parameters relevant to morphology, like wood species and locality, as well as the pulping conditions can considerably influence the runability of the pulp in chemical conversion. But this role of morphology received rather little attention compared with the question of crystallinity, in systematic studies during the last 50 years. Comprehensive investigations emphasizing the relevance of interfibrillar hydrogen bonding on the course of heterogeneous cellulose derivatization have been performed (Schleicher, 1983). A reduction of interfibrillar bonding by suitable pretreatment of the pulp favors a uniform course of reaction. The expression obtained from a quantitative evaluation of the solid state ^{13}C NMR spectra of the pulp was correlated to interfibrillar bonding and employed as an useful indicator of pulp runability in viscose preparation and carboxymethylation (Schleicher et al., 1988). Also, the beneficial effect of many activation techniques (see next section) was assumed to be primarily caused by the splitting of interfibrillar bonds. The sometimes smoother runability of sulfite pulps in comparison with prehydrolyzed sulfate pulps in chemical cellulose processing is obviously closely connected with fibrillar architecture and probably caused mainly by differences in interfibrillar bonding.

The gross morphology of the cellulose starting material can affect the course of heterogeneous derivatization reactions, too, and deserves a brief comment in this context. A controlled disintegration to a rather uniform particle size is frequently a necessary prerequisite to secure well-defined hydrodynamic process conditions and a sufficiently uniform course of reaction. So, for example, alkali cellulose in the form of a pressed sheet or slurry cake requires a shredding to millimeter-sized particles for subsequent uniform oxidative degradation and xanthation. Cotton linters often need a cutting-mill treatment to reduce the fiber length and to avoid spinning of the fibers around the stirring equipment in subsequent processing in suspension. On the other hand, cellulose morphology can be considerably changed during the course of heterogeneous derivatization reac-

tions, e.g. alkali-cellulose formation (Philipp et al., 1989). In this morphometric study, supplying data on size and shape of the cellulose particles after a slurry alkalization, as well as after subsequent shredding, it could be concluded that the percentage of fiber shortening $\Delta L/L \times 100$ increases linearly with the original fiber length. Also the surface roughness of the fibers was definitely enhanced by the alkalization procedure. Tailored procedures have to be elaborated for a chemical modification of cellulose membrane and sorption materials in order to retain the morphology achieved in the previous structure formation.

After considering the effect of the different structural levels on the course of heterogeneous cellulose reactions, the question of accessorial compounds and low molecular by-products shall be raised briefly. Accessorial compounds in the pulp and in process chemicals can seriously impede process stability and product uniformity, and high standards of purity are generally expected today. Hydrophobic compounds on the pulp surface can lead to, for example, a nonuniform course of the nitration process, and may require previous surfactant treatment. A nonuniform and/or varying content of iron ions in a dissolving pulp for viscose preparation inevitably results in a nonuniform 'alkali-cellulose ripening' and subsequently in a deterioration of end-product quality. Besides accessorial compounds present in the starting materials, the formation of low molecular by-products during the reaction itself has to be considered, too. Depending on product end use, sodium glucolates as by-product in CMC can be tolerated in commercial grades, but must be washed out in nutritional and biomedical grades.

2.4.2.3 Activation of cellulose

The problem of enhancing cellulose reactivity is highly relevant to the laboratory-scale organic chemistry of cellulose, as well as to commercial processes of cellulose derivatization. The term reactivity is somewhat ambiguous in so far as it comprises the question of reaction rate, as well as that of ultimate degree of conversion after arriving at a quasi-equilibrium, and the relation to some product properties (like solubility). From the viewpoint of physical chemistry, identification of reactivity with the initial reaction rate of a heterogeneous derivatization seems to be the most tentative and clear cut definition, but is of questionable practical value in commercial cellulose processing. From the site of the polymer, the course of a heterogeneous cellulose reaction is influenced by all structural levels, and *vice versa* all structural levels are affected by this chemical transformation to a varying extent. This mutual interaction largely depends on the type of reaction, the reaction medium and its swelling power, and on external reaction conditions. Thus the reactivity of cellulose is not unambiguously determined by the structure of the starting material, but has always to be considered in relation to the chemical process in question. As a quantitative criterion of reactivity, frequently the initial rate of acetylation has been employed, as this esterification

reaction is rather sensitive to cellulose supramolecular structure. It has to be emphasized once more that the results obtained cannot be transferred to evaluate the performance of cellulose samples in other reactions. As no generalizable criterion of cellulose reactivity can be defined today and obviously does not exist at all, it is necessary to elaborate adequate procedures tailored to the type of reaction in question, which simulate the chemical process as closely as possible, and are centered on the most relevant process or product criterion (for analytical details see chapter 3).

To secure a fast and uniform course of a heterogeneous derivatization with a high degree of conversion, numerous procedures have been elaborated for sample pretreatment in order to decrease crystallinity and interfibrillar bonding and thus to enhance the level and uniformity of accessibility. Two principle strategies have been pursued: one consists of a complete destruction of supramolecular order by dissolving and subsequent reprecipitating the sample in a rather amorphous form, as practised for example by precipitation of cellulose from an aqueous cuprammonium solution into an organic liquid. The high expenditure of manpower and chemicals makes this method suitable for laboratory-scale studies only. The other route is characterized by a loosening of cellulose supramolecular structure with principle preservation of the original solid state of the sample. This route is usually known as cellulose activation. It can be realized either by breaking interchain hydrogen bonds, leading to a spacing of the chains via transient or permanent chemical interactions ('chemical activation'), or by input of energy, resulting in a disordering of the chain molecules at different levels of structure ('physical activation'). Table 2.4.1 presents an overview of both categories of activation procedures.

The most convenient and widely used procedure of activation is the swelling of the sample in a liquid of high swelling power like water, aqueous alkali or DMSO, which may be employed also as the reaction medium. An example is the very fast formation of alkali cellulose with aqueous NaOH of sufficiently high concentration, in comparison with the rather slow reaction with NaOH in ethanol (e.g. Fink et al., 1995). If the swelling agent is not suitable as the reaction medium and for example aprotic conditions are required after swelling in water, a solvent exchange with liquids of decreasing polarity is often a good choice, as the high initial state of swelling is retained fairly well even in a liquid of low swelling power. For 'preswelling procedures' of this kind aqueous alkali or ethanolamine have been successfully employed. To avoid a collapse of the cellulosic pore system on drying, the inclusion of low molecular compounds of high boiling point into the cellulose structure after preswelling has been recommended. Also inhibition with liquid CO_2 with subsequent evaporation has been studied for increasing cellulose reactivity, but positive results published in earlier work could not be confirmed.

The beneficial effects of surfactants in various stages of the viscose process, which were systematically investigated (Schleicher et al., 1967; Schleicher and Philipp, 1968), can probably be traced back to elimination of hydrophobic compounds from the surface, to decreasing interfacial tension between cellulose and the reaction system, and to loosening interfibrillar cohesion.

A very efficient activation of cellulose for subsequent derivatization reactions can be achieved via transient formation of fairly well-defined addition compounds of the polymer. By this method, not only interfibrillar bonds are disrupted but also the crystalline order of cellulose can be significantly decreased by various systems of this kind, especially by aqueous NaOH of sufficiently high concentration or by liquid NH_3. An increase in cellulose accessibility by treatment with a mixture of nitric oxides and acetic acid is reported, based on the development of a capillary system within the fiber (Kapuckij et al., 1979; Sokarros et al., 1982). The use of a bromine water mixture as an activating agent was described, accentuating the role of decrystallization and recrystallization (Lewin et al., 1982).

Table 2.4.1. Routes to cellulose activation

Spacing via intermolecular or covalent interaction ('chemical' methods)	Disordering of structure via energy input ('physical' methods)
Swelling in polar liquids like H_2O, NH_3, EtOH, DMSO	High-energy irradiation like electron beam irradiation; γ-ray irradiation
Inclusion of high boiling liquids like oligoethylene glycols	Heat treatment under defined conditions (120–180 °C, < 1 h)
Surface modification by surfactants	Mechanical disintegration by: shredding; conventional milling in a cutting or attrition mill; ball milling; vibration milling
Transient formation of addition compounds with $NaOH/H_2O$ (mercerization), R_4NOH/H_2O, NH_3 or R-NH_2, N_2O_4/CH_3COOH, Br_2/H_2O	Sonication
Covalent derivatization to low *DS* by grafting with acrylonitrile, etherification with ethylene oxide	
Hydrolytic chain cleavage	

Activation of cellulose by treatment with aqueous NaOH of mercerizing strength is frequently used as a preliminary step in heterogeneous derivatization, especially in combination with a subsequent solvent exchange. After mercerization, the crystalline order is definitely diminished in comparison with the starting material, and also the lattice type is changed from cellulose I to cellulose II. In many subsequent reactions, the effect of disordering dominates, but in some cases the lattice transition showed a negative effect on the course of reaction, resulting in a lower reactivity compared with the original sample of cellulose I. The decrystallization of cotton cellulose by trimethylbenzylammonium hydroxide (aqueous solution), followed by solvent exchange is described as a route to activation (Vigo et al., 1970).

Comprehensively investigated by numerous groups, and amply used in practise as an activating pretreatment for cellulose I, is the interaction with liquid ammonia resulting in the formation of an addition compound (e.g. Hess and Trogus, 1935; Prusakov et al., 1982; see chapter 4.2). The cellulose is regenerated either by washing with water or by evaporation of the NH_3. With both procedures a fairly disordered cellulose is formed, after evaporation of the NH_3, with the lattice type of cellulose III, or after water treatment with the lattice type of cellulose I (Lewin and Roldan, 1972). According to this study, NH_3 is able to penetrate into the cotton-fiber wall, not only along the rings of the S_{II} but also across them. On storage, NH_3-decrystallized cellulose is subjected to recrystallization, especially in the presence of moisture. In processing the activated sample immediately after the treatment, the temperature of activation in the range between –30 and –70 °C can influence the effect of activation. The older literature on NH_3-activation and mercerization has been comprehensively reviewed (Warwicker et al., 1966). With respect to its practical relevance, several variations of cellulose activation with NH_3 have been published during the last decades. The use of gaseous NH_3 under sufficiently high pressure is recommended for cellulose decrystallization to a rather disordered cellulose III, and also lower aliphatic amines have been employed for cellulose activation via the transient formation of an addition compound (e.g. Klenkova, 1967). A very convenient procedure of NH_3 activation was elaborated by employing binary mixtures of NH_3 with a dipolar aprotic liquid like DMF or *N*-methylpyrrolidone (Stein et al., 1992; Wagenknecht et al., 1992a), permitting the handling of the system in the range of temperature between –5 and –15 °C. The NH_3 can be substituted in systems of this kind by lower aliphatic primary amines (Stein et al., 1992).

The effects of a pretreatment with aqueous NaOH on the one hand, and liquid NH_3 on the other, on the structure of cellulose, especially on its accessibility, crystallinity, and morphology have been systematically compared in several studies. A mercerization with NaOH is somewhat more effective regarding a decrease of infrared crystallinity index and an increase of water regain than a pretreatment with liquid NH_3 (Wadsworth et al., 1979). A maximal effect was

observed after a two-step activation of never-dried cellulose with aqueous NaOH and subsequently (after drying) with liquid NH_3.

Employing the spacer effect of substituents, an increase in accessibility and reactivity of cellulose can also be achieved by a rather uniform covalent derivatization, to a low degree of conversion. Examples are the etherification with ethylene oxide to a low *DS* in order to reduce the amount of CS_2 necessary in a subsequent xanthation (Diacik et al., 1977; Fadl et al., 1975). The practical relevance of these procedures, however, is at least questionable, as a further substituent is permanently introduced into the polymer, influencing product properties. This is demonstrated by the finally unsuccessful efforts to reduce CS_2 input into the viscose process by cellulose ethoxylation to low *DS* (Diacik et al., 1977). A reduction in *DP* by hydrolytic chain cleavage can enhance reactivity in some cases, but this activation effect can be counteracted by recrystallization enhancing the supramolecular order.

Activation by input of energy ('physical activation') is always combined with a fairly pronounced chain degradation. Obviously it is not possible to split hydrogen bonds between or within the fibers by input of mechanical energy without cleaving at least some linkages between the monomer units (see chapter 2.3). A rather negligible chain degradation is usually observed after wet beating or sonication of the cellulose fibers, while reduction in *DP* is rather severe after mechanical degradation in a vibrating ball mill.

A special and very effective activation process based on electron-beam irradiation has been developed for enhancing the reactivity of dissolving pulps in the viscose process (Fischer et al., 1985). Besides a moderately controlled chain degradation and an increase in uniformity of chain length distribution, the fibrillar morphology, i.e. the pore and void system of the fiber, is changed by this treatment in a favorable way permitting processing to a viscose spinning solution with a remarkable reduction of CS_2 input.

Application of heat to cellulose, especially on drying from the moist state, usually decreases the reactivity in subsequent chemical transformations due to surface hornification. But, as already mentioned in the previous chapter, a controlled heat treatment of air-dry dissolving pulp in the temperature range between 120 and 180 °C can have a positive effect on subsequent interaction with aqueous NaOH and with CS_2, leading to a better filterability of the viscose solution (Hernadi and Dömötör, 1981; Erdmann et al., 1989; see chapter 2.3).

The routes of activation and their results presented, rather arbitrarily demonstrate the versatility, as well as the specificity, of activation processes. Two conclusions can be drawn:

(i) due to a limited selectivity of bond cleavage, most activation procedures affect all three levels of cellulose structure in the direction of 'a decrease in ordering', with the ratio of structural destruction between the different levels varying widely depending on the procedure employed;

(ii) in agreement with the complexity and system specificity of heterogeneous cellulose reactions, no generally applicable 'optimal activation procedure' is known today and probably cannot be found at all; and a tailoring of the activation procedure to the reaction system is necessary for a fast and uniform course of a heterogeneous derivatization to a desired degree of conversion.

2.4.3 Advantages and limitations of cellulose reactions in DMA/LiCl solution

The previous discussion of cellulose functionalization under heterogeneous and homogeneous conditions raises the general question of advantages and shortcomings of reactions in solution. Some systems of this kind employed rather frequently for different types of reactions are listed in Table 2.4.2 (see also chapter 2.2.2).

Table 2.4.2. Examples of reactions in cellulose solution

Solvent	Reaction
Tetraalkylammonium hydroxides in H_2O	Methylation, xanthation
Butyltriethylammonium chloride in DMSO/pyridine	Acetylation (up to *DS* = 2.6)
N-Ethylpyridinium chloride in the molten state	Acylation (including aromatic compounds), tritylation; addition of CH_2=CH–COOH and of isocyanates
Diethylamine/SO_2/dipolar aprotic liquid	Acylation, benzylation to high *DS*
Amineoxides (e.g. *N*-methylmorpholine-*N*-oxide)/DMSO	Acylation via transesterification with e.g. ethylene glycol diacetates, epoxidation
N,N-dimethylacetamide (DMA)/LiCl, *N*-methylpyrrolidone/LiCl	Acylation; epoxidation, etherification

A broad variety of reactions had been performed already many years ago in melts of *N*-ethylpyridinium chloride (Husemann and Siefert, 1969). Mixtures composed of diethylamine, SO_2, and dipolar aprotic liquids like DMSO were used (Isogai and Ishizu, 1984; Isogai et al., 1986) successfully for esterifications, as well as for etherifications, including reactions with the appropriate aryl and aralkyl compounds. Johnson (1969) described various reactions, especially transesterifications, performed in amineoxide solutions of cellulose. By far the most versatile and interesting system within the nonderivatizing, nonaqueous

cellulose solvents up to now is the binary mixture *N,N*-dimethylacetamide/LiCl or *N*-methylpyrrolidone/LiCl (McCormick and Callais, 1987; Diamantoglou and Kuhne, 1988; Dawsey, 1994).

These media which exemplarely small be treated here in some detail, dissolve even high molecular cellulose (*DP* > 1000) completely after preactivation at a LiCl concentration of 7–9 % by weight. Suitable procedures for preactivation are decrystallization with liquid NH_3 or swelling in an aqueous system with subsequent solvent exchange. A pretreatment by mercerization with 20 % NaOH for 4 h was reported by Diamantoglou and Kundinger (1995) to be of peculiarly high efficiency. At a *DP* of 600, cellulose solutions up to 12 wt% concentration could be prepared, if a LiCl-to-AGU molar ratio of at least 3 was secured. According to present knowledge, the solvent system acts via formation of a Li^+ cation with several DMA molecules bound as ligands at the carbonyl oxygen and the Cl^- associated with a hydrogen atom of the cellulose (see Fig. 2.2.12 and chapter 4.3).

Advantages claimed for DMA/LiCl solutions in homogeneous reactions of cellulose are a full availability of hydroxy groups, permitting control of the *DS* via the reagent to AGU molar ratio, a minimal chain degradation at a temperature below 100 °C, a high versatility with regard to the type of reaction intended and a favorable reagent yield due to rather small consumption for side reactions. The latter statement, however, must be viewed relatively in so far as the Cl^- present at rather high concentration frequently acts as a competitive nucleophile to the cellulosic hydroxy groups with their rather low nucleophilicity (Dawsey, 1992; Rahn et al., 1996). Furthermore, a low solubility of either one of the reaction components or of the reaction product in the medium can possibly limit the degree of conversion achieved. All these statements hold true also for the *N*-methylpyrrolidone/LiCl system, with the *N*-methylpyrrolidone being considered to be somewhat less toxic than DMA.

The solvent system proved to be very efficient and versatile in homogeneous cellulose esterification, and many reactions of the dissolved polymer with acylchlorides or acylanhydrides of mono- and dibasic acids, including aromatics ones, have been reported in the relevant literature (e.g. Table 2.4.3).

The maximal *DS* obtained often exceeds a value of 2, but obviously remains below 3 in almost all the studies so far reported, even at a large excess of reagent. A reagent yield of 80–85 % could frequently be realized in these acylation reactions. Some of the catalysis methods employed in cellulose esterification in DMA/LiCl are (Diamantoglou and Kundinger, 1995):

- acid catalysis, e.g. $HClO_4$, $CH_3{\cdot}SO_3H$, H_2SO_4, HCOOH;
- salt catalysis, e.g., alkali acetates;
- basic catalysis, e.g., triethylamine, pyridine, dimethylaminopyridine, and dicyclohexylcarbodiimide.

Table 2.4.3. Examples of cellulose esterification in DMA/LiCl solutions

Cellulose ester	Reagent	DS_{max}	References
Acetate	Ac_2O/TEA	2.85	Diamantoglou and Kuhne, 1988
Acetate	Ac_2O, AcCl	2.4	McCormick and Callais, 1987
Propanoate	RCOCl/TEA	2.6	McCormick and Callais, 1987
Octanoate	RCOCl/TEA	2.2	McCormick and Callais, 1987
Benzoate	RCOCl/pyridine	2.8	McCormick and Callais, 1987
Phenylacetate	RCOCl/TEA	2.8	McCormick and Callais, 1987
Cinnamate	RCOCl/pyridine	3.0	Ishizu et al., 1991
Phthalate	$(RCO)_2O$	1.3	Diamantoglou and Kuhne, 1988
Maleate	$(RCO)_2O$	1.1	Diamantoglou and Kuhne, 1988
Succinate	$(RCO)_2O$	1.0	Diamantoglou and Kuhne, 1988
Phenylcarbamate	Phenylisocyanate/pyridine	2.0	McCormick and Callais, 1987
Tosylate	TosCl/TEA	2.4	McCormick and Callais, 1987; Rahn et al., 1996
Sulfate	SO_3·DMF/TEA	0.6	Wagenknecht et al., 1985

TEA, triethylamine; R, corresponding organic residue.

Triethylamine proved to be superior to pyridine in esterification with acylchloride, with respect to the higher acidity of pyridine hydrochloride promoting chain degradation and often an undesired split-off of substituents. With acid anhydrides as esterification agents, an order of reactivity of acetyl anhydride > phthalic anhydride > maleic anhydride > succinic anhydride was observed (Diamantoglou and Kuhne, 1988). The half-ester sodium salts of the phthalic, maleic and succinic acids were found to be water soluble already at a *DS* of 0.45. Also esters with long side chains have been prepared in DMA/LiCl. The reaction with stearyl chloride in the presence of triethylamine yielded a mixture of normal and ketoester obviously formed via a ketene-like intermediate (Diamantoglou and Kundinger, 1995). Esterification with some inorganic acid chlorides and anhydrides has been studied too, but with limited success only due to rather violent side reactions and an early precipitation of the reaction products. Wagenknecht et al. (1985) reported sulfation of cellulose dissolved in DMA/LiCl with the SO_3·DMF complex up to a *DS* of 0.35. The degree of esterification obtainable can be limited by precipitation of the reaction product already at a moderate *DS*. This was observed with the phthalic half-ester of cellulose due to formation of an insoluble triethylamine salt. A further limitation is caused by the above mentioned competition of Cl^- from the solvent system as a nucleophile, as seen in the study on cellulose nitrite formation with N_2O_4. This resulted in complete esterification to *DS* values of 3 in N_2O_4/DMF, but did not

exceed a *DS* value of 1.4 in DMA/LiCl even at a large excess of N_2O_4 (Wagenknecht et al., 1992b). Of some interest from the mechanistic point of view is this competition for the alternative formation of cellulose tosylate and of chlorodesoxycellulose on reacting cellulose in DMA/LiCl with tosyl chloride in the presence of triethylamine. At a reaction temperature below 8 °C cellulose chlorination was found to remain well below a *DS* of 0.1, and at a *DS* of 2.4 for the tosylester groups (Rahn et al., 1996), while at 50 °C and 70 °C chlorination dominated by far (see Fig. 2.4.11).

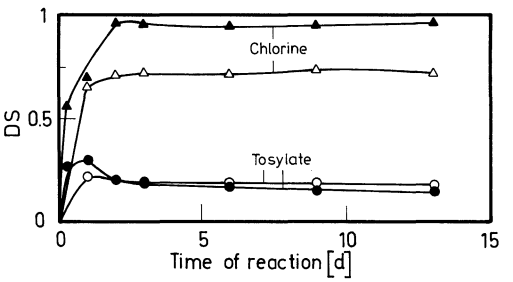
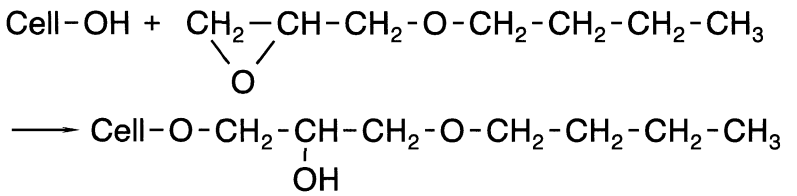


Figure 2.4.11. Course of formation of cellulose tosylate and chlorodesoxycellulose at 50 °C (Δ, ○) and 70 °C (▲, ●), molar ratio Cell-OH : TosCl : TEA = 1 : 1.5 : 2 (d = days).

According to Dawsey (1994) the chlorination occurs in competition with esterification via an intermediate formation of a formiminium salt (Vilsmeyer reaction) as shown schematically in Fig. 2.4.12.

Etherification of cellulose in DMA/LiCl generally proceeds with much more difficulty than esterification. A high excess of reagent and long reaction times of up to 3 days are usually needed to arrive at high *DS* values. As a base necessary as a catalyst or in a stoichiometric amount, most frequently powdered NaOH has been employed.

Under comparable conditions of reaction, with a rather low molar ratio of agent and base to AGU, etherification by ring opening addition, e.g. a hydroxyethylation, proceeds to a much higher *DS* than for example a carboxymethylation or a methylation requiring one equivalent of base per mole of ether groups. Water-soluble cationic cellulose ethers with *DS* values above 2 were synthesized (Ott et al., 1989) with a large molar excess (>10 mol/mol of AGU) of glycidyltrimethylammonium chloride at 70 °C. The DMA/LiCl solvent system was used in (Nishimura et al., 1997) to prepare a comb-shaped amphiphilic cellulose ether by a reaction of the dissolved cellulose with butyl glycidyl ether to a molar substitution of 0.4-1.0 coressponding closely to the appropriate DS, according to the scheme



The water soluble ether showed a reversible thermal sol-gel transition in aqueous solution and surface activity.

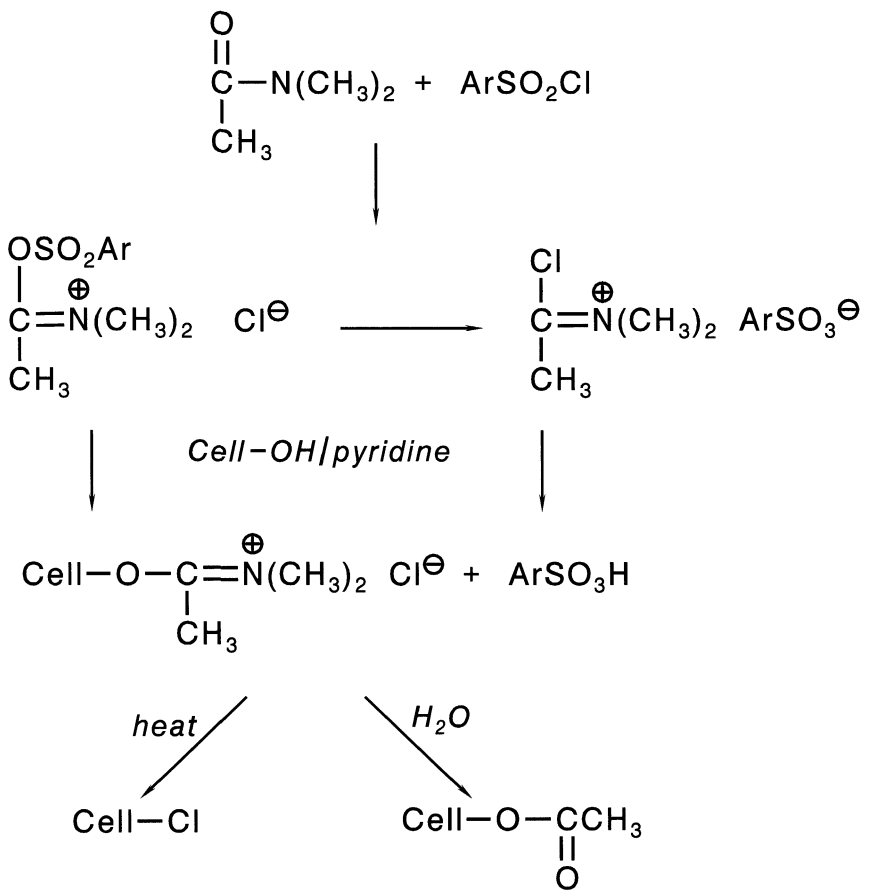


Figure 2.4.12. Scheme of formation of chlorodesoxycellulose on tosylation of cellulose dissolved in DMA/LiCl (Dawsey, 1994).

Table 2.4.4. Etherification of cellulose in DMA/LiCl solution (details see chapter 4.5)

Cellulose ether	Reagent	Mol. reagent/ mol. AGU	Base	*DS*	References
Methyl	CH_3I	1.5 : 1	NaOH	< 0.1	Diamantoglou and Kuhne, 1988
	CH_3I	1 : 1	NaOH	1.1	McCormick and Callais, 1987
Hydroxypropyl	Propylene oxide	1.0 : 1	NaOH	0.48	Diamantoglou and Kuhne, 1988
Carboxymethyl	Chloroacetic	1.5 : 1	NaOH	< 0.1	Diamantoglou and Kuhne, 1988
	acid	1.5 : 1	LiOH	< 0.1	Diamantoglou and Kuhne, 1988
	Chloroacetic acid (Na salt)	4 : 1	NaOH	1.7	Heinze et al., 1994
Benzyl	Benzyl chloride	–	NaOH	2.3	McCormick and Shen, 1982; Isogai et al., 1984
Trityl	Trityl chloride	3 : 1	Pyridine	1.2	Camacho Gómez et al., 1996
Trimethylsilyl	Trimethylsilyl chloride	6 : 1	Pyridine	2.9	Schempp et al., 1984; Stein, 1991
Thexyldimethyl-silyl	Thexyldimethylsilyl chloride	3 : 1	TEA	1.9	Koschella and Klemm, 1997
O-(2-hydroxy-3-trimethyl-ammo-nium)propyl	2,3-Epoxipropyl-trimethylammonium chloride	1.0 : 1	NaOH	0.42	Diamantoglou and Kuhne, 1988

TEA, triethylamine.

Also a carboxymethylcellulose with a *DS* of up to 1.7 was obtained (Heinze et al., 1994) with a sufficiently great excess of monochloroacetic acid and powdered NaOH after a reaction time of up to 72 h, taking into account a considerable chain degradation. Methylation at the medium-to-high *DS* level was performed with an excess of methyl iodide. With a series of alkyl iodides, the *DS* obtained under preset conditions of reaction was found to decrease from the methyl to the butyl ether. Isogai et al. (1986) reported the preparation of a benzylcellulose with a *DS* of 2.8, employing benzyl chloride as the agent and potassium *tert*-butanolate or sodium hydroxide.

In a recent study the effect of methoxy substitution of diphenyl- and triphenylchloromethanes on the etherification was investigated (Erler et al., 1992; Camacho Gómez et al., 1996). The maximal *DS* value for triphenylchloromethanes obtained was in all cases at a level of 1.0, with high 6-O regioselectivity in the case of tritylation (see chapter 4.5.4).

A homogeneous silylation of cellulose was performed with trimethylsilyl chloride and triethylamine up to a *DS* level of 2.7–2.9 and with thexyldimethylchlorosilane and triethylamine to *DS* values of 1.9 (see chapter 4.5.5).

Referring again to the competing nucleophilic action of the chloride ions present in DMA/LiCl, it seems worth mentioning that with propanesultone no etherification could be achieved due to formation of 3-chloropropane sulfonate not reacting with the polymer, while with ε-caprolactone, the ring cleavage at the carbonyl group resulted in an esterification of cellulose up to a *DS* of 0.8 (Fig. 2.4.13).

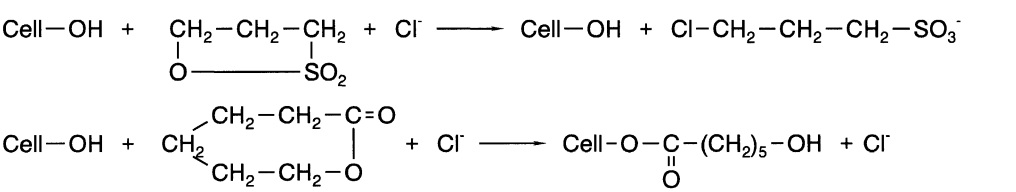


Figure 2.4.13. Reaction of the ring systems of propanesultone and ε-caprolactone in DMA/LiCl/cellulose.

Isocyanates react smoothly with cellulose in DMA/LiCl in the presence of a suitable base like pyridine, resulting in a *DS* of 2.55 with phenylisocyanate and in a *DS* of 1.95 with *p*-toluene isocyanate (Terbojevich et al., 1995). Also acetalization to high *DS* (Suzuki et al., 1992) and chlorination to chlorodesoxycellulose with chloro-*N*-succinimide and triphenylphosphine or bromination with tribromimidazol/triphenylphosphine can be realized in the DMA/LiCl system (Furuhata et al., 1992; Furuhata et al., 1995).

Compared with most homogeneous reactions performed with cellulose dissolved in DMA/LiCl, information on distribution of functional groups within the AGU is rather scarce.

It can be concluded that the regioselectivity is rather limited if unsubstituted cellulose and not an already regioselectively modified intermediate is employed as the starting material. The 6-position is generally the preferred site of reaction and can be the only one in the low *DS* range up to 0.5. A rather high 6-selectivity was observed with the voluminous triphenylmethyl group.

In conclusion, it can be stated that DMA/LiCl as a nonderivatizing cellulose solvent is very suitable for studying new cellulose reactions and for elucidating reaction pathways under well-defined conditions, but that with the exception of tritylation it is not a good route for regioselective functionalization within the AGU. It is promising, however, for realizing unconventional substituent distributions along the polymer chains by means of a low molecular reaction component present in the solid state, as demonstrated recently by synthesis using solid NaOH as the template, which yielded reactive microstructures. The products obtained show a nonstatistical distribution of the differently functionalized repeating units (Liebert and Heinze, 1997).

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3 Analytical Methods in Cellulose Chemistry

Before describing systematically the various categories of cellulose reactions and important synthesis pathways to functionalized cellulose in chapter 4 of this book, it seems appropriate to present an overview on the analytical techniques employed today in cellulose chemistry. A fast and reliable supply of comprehensive analytical data is an indispensable prerequisite for considering and pursuing new routes of synthesis and for controlling chemical processes in cellulose functionalization. This holds true for elucidating or controlling the course of reaction, as well as for characterizing a new or an established cellulose product.

This overview will be completely application-minded, considering possibilities and limitations in practical use, without going into the details of fundamentals of the techniques in question, or describing details of the instruments employed. Modern instrumental techniques, as well as so-called classical chemical methods, will be adequately considered with equal relevance, as both these categories play an important role in laboratory-scale work, as well as in commercial processes and product control. Besides the constitution and the chain length of the macromolecules, the state of dispersion of the systems involved and also the characterization of supramolecular and morphological structure of starting materials and products will be given due regard.

Just as in general polymer analysis, a trend toward a combination of different techniques for comprehensively describing complex structures, a growing interest in adequately automated methods with computerized data processing, and strong efforts to substitute or at least to complete 'averages' by 'distribution patterns' as analytical output, are characteristic in cellulose research, too. Peculiar demands on the analyst arise from the necessity to describe quantitatively the distribution of substituents within the AGU, as well as along and between the polymer chains, to assess intermolecular interactions both in the solid state and in liquid systems, and to analyze small amounts of functional groups and by-products in the starting material, as well as in cellulose products, and to supply these data as far as possible not only as overall averages but also including their spatial distribution.

As the chemical transformation of cellulose usually starts from the fibrous state and frequently ends with artificial fibers or films, a complex surface analysis, is rapidly gaining acceptance and promotes the application of modern optical techniques.

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D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht

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For a brief and streamlined presentation of the complex and diversified area of cellulose research, the following systematic arrangement of topics is considered appropriate:

–determination of the degree of polymerization
–chemical analysis (elemental and functional group analysis)
–application of instrumental analysis for assessing the molecular structure and intermolecular interactions
–fractionation and separation procedures
–summary of techniques for the determination of the degree of substitution and the substituent distribution
–methods for characterizing the state of dispersity/state of solution of cellulosic systems
–abridgment of methods for the characterization of cellulose supramolecular and morphological structure in the solid state

The chapter will be finalized by a short outlook on future developments in cellulose and relevant polymer analysis.

3.1 Determination of the Degree of Polymerization of Cellulose and its Derivatives

All samples of cellulose and its derivatives, even those resulting as fractions from a separation procedure according to molar mass, show polydispersity with

F_1: $M_1 = 1000$ $n_1 = 1$

F_2: $M_2 = 200$ $n_2 = 5$

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \qquad M_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$M_w = \frac{10^6 + 2 \cdot 10^5}{10^3 + 5 \times 2 \cdot 10^2} = 600 \qquad Mn = \frac{1000 + 1000}{1 + 5} = 333$$

$$U = \frac{M_w}{M_n} - 1 = 0{,}8$$

Figure 3.1.1. Illustration of the mean of M_w, M_n and U by a model polymer of two fractions F_1 and F_2.

regard to their molar mass or degree of polymerization (*DP*), i.e. they consist of macromolecules differing in the number of repeating units. This implies a difference between the weight-average molecular mass (M_W) and the number-average molecular mass (M_n), with $M_W > M_n$ and a nonuniformity parameter $U > 0$ (Fig. 3.1.1).

M_n or DP_n values are adequate in dealing with cellulose degradation, while M_W or DP_W frequently show a better correlation to product properties.

Among the methods described in text books on the physical chemistry of polymers for determining molar mass averages without additional assumptions and without calibration, light scattering, supplying M_w values, and sedimentation/diffusion measurements, delivering approximately M_w, are used in scientific cellulose research. In case of cellulosics of rather low molecular mass, the classical membrane osmometry as an absolute method for obtaining M_n values today is widely abundant and substituted by vapor pressure osmometry. This technique makes use of the temperature difference between polymer solution and an ambient saturated solvent vapor atmosphere with this δT corresponding to the osmotic pressure of the solute, but requiring a calibration with samples of known molar mass. The formula connecting analytical signal and molar mass are summarized in the scheme in Fig. 3.1.2.

For details on fundamental and practical applications of these techniques the reader is referred to the appropriate text books, e.g. Vollmert (1962); Arndt and Müller (1996).

Light scattering

$$\frac{1}{M_n} = \lim_{\substack{c\to 0 \\ \vartheta\to 0}} \frac{K\times c}{I_{red}} \qquad \text{reduced scattering intensity}$$

$$I_{red} = \frac{I(\vartheta)\times R^2}{I_0 \times V_0} \times \frac{1}{1+\cos^2\vartheta} \qquad K = \frac{2\pi^2 n_0^2}{N_L \times \lambda^4} \times \left(\frac{dn}{dc}\right)^2$$

ϑ = scattering angle; R = distance from scattering volume to detector; v = scattering volume; n = refractive index; c = polymer concentration; N_L = Avogadro's number; λ = wavelength of light source.

Sedimentation/diffusion

$$M_w = \frac{RT\times s}{D(1-\rho v)} \qquad s = \frac{dx}{dt}/\omega^2 x$$

s = sedimentation coefficient; D = diffusion coefficient; x = distance from rotor; v = specific volume of polymer dissolving; ρ = density of solvent; ω = angular velocity.

Vapor pressure osmosis

$$\frac{1}{M_n} = \lim_{c \to 0} \frac{\overline{\Delta T}}{c} \times \frac{1}{K_c}$$

$\overline{\Delta T}$ = difference in temperature between polymer solution and solvent atmosphere
K_c = calibration constant obtained with samples of known M_n

Figure 3.1.2. Formulae for the calculation of molar mass averages from light scattering, sedimental-diffusion and vapor pressure osmometric measurements.

For practical use in laboratory-scale organic chemistry of cellulose, as well as in process and product control of commercial cellulose functionalization, generally viscosity measurements are employed for the determination of molar mass or degree of polymerization. These 'viscosity techniques' are based on the fundamental law of Staudinger–Kuhn–Mark–Houwink

$(\eta) = K \cdot M^{\alpha}$ and $(\eta) = K' \cdot DP^{\alpha}$

and require a primary calibration with samples of known molar mass. They provide a so-called viscosity-average M_V or DP_V which usually does not deviate much from M_W or DP_W. The intrinsic viscosity $[\eta]$ is usually obtained from the efflux time of a dilute polymer solution in the concentration range below 1% in a capillary viscometer in relation to that of the pure solvent used. The route of calculation is indicated in the scheme in Fig. 3.1.3.

Schulz–Blaschke	system-dependent constant
$\eta_{spec}/c = [\eta] + k_{SB} \cdot [\eta] \cdot \eta_{spec}$	k_{SB}
Huggin $\eta_{spec}/c = [\eta] + k_H \cdot [\eta]^2 \cdot c$	k_H
Martin $\ln(\eta_{spec}/c) = \ln[\eta] + k_M \cdot [\eta]^2 \cdot c$	k_M

Figure 3.1.3. Formulae frequently employed for the calculation of the intrinsic viscosity $[\eta]$ from a 'single point' measurement of η_{spec}/c (see also Fig. 3.1.4.).

For precision measurements, a double extrapolation of the reduced viscosity η_{spec}/c to zero concentration and zero shear is required but with sufficiently long efflux times $t > 100$ s (H_2O) the shear dependency can be neglected for routine measurements. The extrapolation to zero concentration of polymer can be per-

formed either by a series of measurements at different polymer concentrations, usually in an automated dilution viscometer, or via a one-point measurement at a sufficiently low polymer concentration, with subsequent calculation of (η) according to one of the formulae listed in Fig. 3.1.4.

Relative viscosity η_{rel} = efflux time of solution t_1/efflux time of solvent t_0

Specific viscosity $\eta_{spec} = \eta_{rel} - 1 = \frac{t_1 - t_0}{t_0}$

Reduced viscosity $\eta_{red} = \frac{\eta_{spec}}{c}$ c = polymer concentration

Intrinsic viscosity $[\eta] = \lim_{c \to 0} \frac{\eta_{spec}}{c}$ $[\eta] = K_M \times M_v^{\alpha} = K'_M \times DP_v^{\alpha}$

$$\log M_v = \frac{\log[\eta] - \log K_M}{\log \alpha} \qquad \log DP_v = \frac{\log[\eta] - \log K'_M}{\log \alpha}$$

Figure 3.1.4. Scheme of viscosity-average M_V and DP_V calculation from viscosity measurements.

An application of this general procedure to cellulose requires a dissolution of the polymer in a suitable solvent (see Table 3.1.1) or a complete (or approximately complete) derivatization, conventionally to the nitrate (Lukanoff and Philipp, 1966) or carbanilate (Gröbe, 1989), with subsequent dissolution in a suitable organic liquid.

The constants K and α of the Staudinger–Kuhn–Mark–Houwink formula, characterizing the hydrodynamic interaction between polymer and solvent, depend, of course, on both components of the system, and are listed for media frequently used in cellulose characterization in Table 3.1.1 and 3.1.2. A detailed procedure describing the determination of *DP* of cellulose in the conventional metal-complex solvent Cuam is presented in the Appendix at the end of Vol. 1.

With partially functionalized celluloses, the problem of the dependency of K and α on the *DS* values arises. Sometimes it can be overcome by splitting-off the substituent without significant chain degradation and subsequent determination of *DP* of the unsubstituted cellulose sample by conventional techniques. In the case of cellulose esters of limited stability like cellulose acetate or cellulose xanthogenate this procedure can be suitable. Dealing with rather stable derivatives like cellulose nitrate, CMC or methylcellulose, the dependency of K and α on the degree of substitution must be determined experimen tally via a so-called

Table 3.1.1. Solvents frequently employed for the determination of the DP of cellulose and cellulose esters and the appropriate parameters K, α, kSB and [η] (Lukanoff and Philipp, 1966; Linow and Philipp, 1970; Gröbe, 1989)

Solvent	K-M-H[a]		Range of $[\eta]x10^{-2}$	k_{SB}[b]
	K x 10^{-2} (ml/g)	α		
Cuam	11.33	0.657″	0.2-	0.29
	10.1	0.661	0.2-4	
Cuen	0.498	1.0″	1-2.4	0.29
	0.395	1.0″	2.4-21.4	
	0.334	1.0	<10	
Cadoxen[c]	0.435	1.0″	0.5-	0.29
	0.7585	0.96	1.9-6.5	
FeTNa[c]	0.907	1.0	-	0.33
DMA/LiCl[c]	0.01278	1.19	-	-
Cellulose nitrate/acetone	0.282	1.8″	<12	-
	0.863	0.91″	3.9-50	
	0.173	1.0″	1.23-30.3	
	0.377	0.95	0.9-18	
	1.66	0.86	1.7-5.2	
Cellulose tricarbanilate/acetone	0.143	0.91″	-	-
	0.466	0.84	-	

a Kuhn-Mark-Houwink equation. b Schulz-Blaschke constant. c KM on molar mass basis (McCormick et al., 1985).

'absolute method' like light scattering. Obviously, so far no tentative relation between intrinsic viscosity and degree of substitution could be established for derivatives of this kind within a wide *DS* range. A reason for this is the rather ill-defined changes in the state of the solution with *DS*, arriving at strong deviations from the 'molecularly dispersed state', especially in the low *DS* range.

Table 3.1.2. [η]-DP-relation for cellulose in metal complex solvents (range of DP between 600 and 11800, based on corresponding cellulose carbanilates) (Linow and Philipp, 1970).

Solvent	[η]-DP relation (ml/g)
Cuam	$[\eta]=1.37 \times DP^{0.72}$
Cuen	$[\eta]=1.67 \times DP^{0.71}$
Cadoxen	$[\eta]=1.75 \times DP^{0.69}$
FeTNa	$[\eta]=4.85 \times DP^{0.61}$

In routine work, sometimes the solution viscosity of a cellulose derivative in a given solvent at a defined concentration of e.g. 1% of polymer, measured in a prescribed type of viscometer, is employed as an index of *DP*. This time saving route may be justified for a first orientation, if it is limited to a comparison of samples of the same type of chemical structure and if it is kept in mind that no tentative linear correlation exits between this solution viscosity and the real *DP* of the sample.

3.2 Chemical Analysis (Elemental Analysis and Functional Group Analysis) of Cellulose and Cellulose Derivatives

Today's conventional automated semimicroelemental analysis, consisting of high-temperature combustion of the sample in a stream of helium and oxygen, with subsequent quantitative detection of CO_2, H_2O, SO_3 and N_2, can usually be employed without problems for cellulose and its derivatives for a reliable determination of the content of C, H, S and N. Problems can arise, of course, in handling of a small sample of unstable cellulose derivatives, for example cellulose nitrite, where a determination of the ester content by functional group analysis (see below) is more favorable. With sodium cellulose sulfates, the classical combustion frequently yielded too low sulfur contents. For assessing the phosphorus content in relevant cellulose products, a wet combustion with HNO_3 and

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subsequent emission spectrophotometric determination of the phosphoric acid (at a phosphorus content above 10 ppm of the sample), or a classical gravimetric determination via precipitation with ammonium molybdate (at higher phosphorus contents, above 1%) can be recommended. The silyl content of trialkylsilyl ethers of cellulose can be favorably determined by a wet combustion with H_2SO_4 or H_2SO_4/HNO_3 and subsequent weighing of the residue before and after treatment with hydrofluoric acid (Stein, 1991; Schuldt et al., 1994). The reliability of the results obtained depends largely on details of the wet combustion procedure in order to secure a complete destruction of organic matter on the one hand and to avoid a loss of silica via the fumes evolved on the other. This is demonstrated in Fig. 3.2.1 by a comparison of a conventional wet combustion method and a technique especially adapted to cellulose silyl ethers.

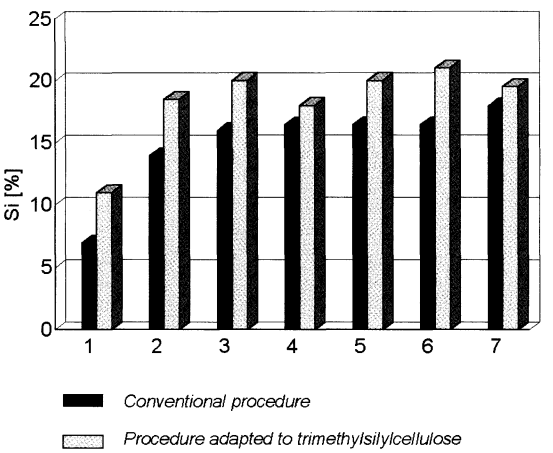


Figure 3.2.1. Comparison of wet-combustion procedures for the determination of the Si content of cellulose silyl ethers 1–7.

The silylcellulose-tailored procedure obviously avoids losses of SiO_2 and yields a higher SiO_2 residue with a high accuracy.

The halogen content, especially the chlorine content of chlorodesoxycelluloses, can be reliably and quickly assessed by combustion in a stream of oxygen and subsequent argentometric titration of the chloride ions. For the determination of small amounts of inorganic impurities, especially of metal ions in dissolving pulps, national and international tentative procedures do exist which usually start with a dry combustion of a rather large (5 g) sample and to which the reader is referred for further details (Zellcheming Merkblätter IV/40/77; IV/41/67, Darmstadt, Germany).

The content of alien polysaccharides in dissolving pulps as the starting material for derivatization, for example the content of xylan or of manan, is usually determined today by chromatographic techniques (see later in this chapter). As a classical chemical method, the determination of the pentosan content via its transformation to furfural with hydrobromic acid and subsequent bromatometric titration of the furfural, is still widely used (Zellcheming Merkblätter IV/40/77; IV/41/67). Oligomer and low-*DP* cellulose and other polysaccharides ('hemicelluloses') in aqueous and aqueous alkaline extracts of pulp are determined by wet combustion with $K_2Cr_2O_7/H_2SO_4$ and back titration of excess Cr^{6+} (see the Appendix at the end of Vol. 1).

Turning now to the determination of functional groups in cellulose and its products, rather specialized procedures are required here, tailored to the structural type and the level of concentration in question. Thus only a limited number of groups of commercial or scientific interest can be considered in this overview.

In dissolving pulp, the assessment of the small amount of carboxyl and carbonyl functions present here is of special relevance. Carboxyl groups may disturb subsequent processes of fiber spinning or film casting via the binding of polyvalent cations, and carbonyl functions can induce chain degradation especially in alkaline media.

The content of carboxyl groups covering the range between 10 and 40 mmol kg^{-1} in dissolving pulps from wood, and about 2 to 10 mmol kg^{-1} in linters, is determined either by a special alkalimetric titration after converting the carboxylate functions to free COOH groups, or via the binding of suitable cations, assessing the amount bound or the decrease in concentration in the ambient solution. Both these principles are realized in heterogeneous systems, i.e. an aqueous suspension of the cellulose fibers, raising the problem of complete accessibility. It could be certified, however, by titration under homogeneous conditions, after dissolving the cellulose samples in a suitable nonderivatizing nonaqueous solvent consisting of DMSO, methylamine and ethanol amine, that about 85 to 100 % of the total carboxyl group content is available to the reagent also in the heterogeneous routes of determination (see Table 3.2.1).

For a fast and reliable routine determination of the content of carboxyl groups in pulps, a modified 'methylene blue method' is widely used and can be fully recommended. It is based on the binding of the methylene blue cation to the COOH functions and a subsequent determination of the decrease in dye concentration in the surrounding solution. A detailed experimental procedure is presented in the Appendix at the end of Vol. 1. The rather small amount of carbonyl functions of usually 10 to 20 mmol kg^{-1} in sulfite pulps and less than 5 mmol kg^{-1} in prehydrolyzed sulfate pulps is conveniently determined by reacting these groups with hydroxylamine to the corresponding hydroxamic acid after a treatment with Zn^{2+} ions and subsequent determination of the nitrogen content of the purified sample by elemental analysis. The treatment with Zn^{2+}

ions is necessary to destroy lactone rings and to convert their carboxyl groups into the Zn salt (Rehder, 1963). According to our experience, the determination of carbonyl functions via hydroxamic acid is more favorable than the reaction with hydrazine. A separate determination of keto groups can be performed by the same procedure after previously oxidizing the aldehyde groups to carboxyl groups with a mild oxidant, e.g. sodium chlorite.

Table 3.2.1. Comparison of various methods of carboxyl group determination in cotton linters and wood pulp (compiled from Schleicher and Lang, 1994; Dautzenberg and Philipp, 1974)

Sample	mmol of COOH/kg of sample		
	Methylene blue sorption	Alkalimetric titration heterogeneous	Alkalimetric titration homogeneous
Cotton linters	6.8	4.5	–
Prehydrolyzed sulfate pulp	17.4	14.5	–
Beech sulfite pulp	27.0	27.0	–
Cellulose/NaOCl	32.9	32.4	–
Cellulose/NaOCl	–	52	29–78
Cellulose/$NaIO_4$/NaOCl	–	222	290
Cellulose/$NaIO_4$/NaOCl	–	492	465

The principles outlined here can be employed also to analyze the carboxyl and carbonyl contents of oxidized celluloses. The degree of oxidation of carboxycellulose obtained by oxidation with nitric oxides can be determined without problems either by dissolving the sample in dilute aqueous alkali and titrating the excess of NaOH with acid, or by a direct titration of the sample in aqueous suspension with 0.1 M aqueous NaOH, using a potentiometric endpoint detection (Heinze et al., 1990). In the latter case the rate of titrant addition must be slow enough to secure a stable potential near the end point, giving due regard to the time required for titrant diffusion into the particles.

Although the *DS* of cellulose ethers and esters is frequently obtained today by instrumental analysis, especially by ^{13}C NMR spectroscopy, elemental and/or functional group analysis is still of consequence for calibration and reference, as well as for a check up performed directly at the organic chemist's bench. Turning first to cellulose ethers, the *DS* of methylcellulose can be assessed by a modified Zeisel–Vieböck method. It consists of a cleavage of the ether bond by heating with hydroiodic acid, distilling-off quantitatively the CH_3I formed, and determining the iodine content after oxidation to iodate by an iodometric titration. This method of methoxy group determination is very reliable and rather

fast if performed with a sufficiently large number of samples, but requires considerable skill and experience. After adequate adaptation, this technique of ether bond cleavage can also be applied to ethylcellulose and higher alkyl ethers of this polymer, and also to hydroxyalkylcelluloses like hydroxyethyl or hydroxypropylcellulose. In the latter case, however, it has to be considered that not only the ether bond to the cellulose backbone but also the ether bonds of the oligoglycol side chains are cleaved, resulting in the determination of the total number of the hydroxyalkyl units (MS) bound to the polymer rather than in the determination of a real *DS* value. The results obtained by ether cleavage therefore must be supplemented by a selective and quantitative esterification of the hydroxy groups of the side chains, for example by reaction with phthalic anhydride in pyridine and subsequent determination of the ester content.

The *DS* of carboxymethylcellulose, ranging from about 0.5 to 1.0 in commercial samples, but being above 2 in laboratory-scale procedures, can be determined by different techniques via the cation binding of the anionic carboxyl group. In highly purified Na-carboxymethylcellulose a gravimetric determination of the sodium content as Na_2SO_4 after wet combustion with H_2SO_4 supplies very reliable values over a wide range of *DS*. As a standard method, often the precipitation of the insoluble uranyl salt of CMC with subsequent gravimetric determination of the uranium oxide (U_3O_8) content is recommended, which according to our experience is very precise due to the high atomic weight of uranium, and is very reliable in the *DS* region up to 1.0, but shows negative deviations from the true *DS* values with highly carboxymethylated samples due to incomplete cation binding obviously caused by steric hindrance (Fig. 3.2.2 and Francis, 1953).

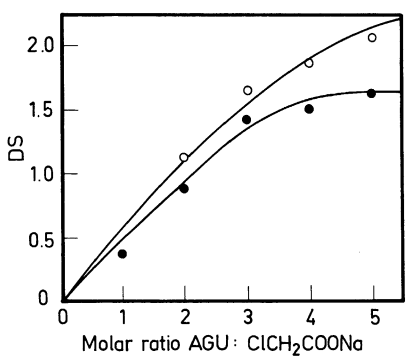


Figure 3.2.2. Comparison of the *DS* values of carboxymethylcellulose samples obtained by gravimetric analysis with uranyl nitrate (•), and by HPLC (o) after chain degradation (see chapter 4.5.2.2) for comparison (Heinze et al., 1994a).

As a fast, routine method, especially for commercial samples, a colloid titration with a cationic polyelectrolyte or a cationic surfactant is frequently employed. As detailed in the experimental procedure presented in the Appendix of Vol. 1, the endpoint detection is accomplished here visually by observing the point of flocculation (Hong et al., 1978).

The ether content of triphenylmethylcelluloses can be determined gravimetrically after conversion of the triphenylmethyl group to the corresponding carbinol by reaction with concentrated sulfuric acid (Green, 1963). The results of this functional group analysis are in good agreement with those obtained by elemental analysis, as illustrated in Table 3.2.2.

Table 3.2.2. Comparison of two analytical techniques for determining the *DS* values of triphenylmethylcelluloses

Sample	*DS* by elemental analysis	*DS* by gravimetry[a]
1	0.41	0.43
2	0.61	0.67
3	0.92	0.83
4	1.05	1.12

[a] Hydrolysis with H_2SO_4 and isolation of the triphenylmethyl carbinol (Green, 1963).

The content of acetyl groups in cellulose acetate as a typically and commercially relevant carbonic acid ester of cellulose can be obtained either by acid or by alkaline saponification and subsequent titration of the acetic acid liberated (and distilled-off) or by titration of the excess alkali not consumed in sodium acetate formation. The route of alkaline saponification is generally practised as a fast and convenient procedure, which is described in detail in the Appendix at the end of Vol. 1. This method can easily be adapted to determine the *DS* values of higher carbonic acid esters of cellulose, as well as of cellulose formates (Philipp et al., 1990).

The *DS* values of esters of cellulose with common mineral acids, i.e. H_2SO_4, H_3PO_4, and HNO_3, can be obtained by elemental analysis of the heteroatoms S, P, and N. But procedures of functional group analysis are available, too, for anionic cellulose sulfates and for cellulose nitrate, and are rather frequently used. For cellulose sulfuric acid half-esters, several routes can be considered, i.e. a colloid titration with a suitable cationic polyelectrolyte, taking the flocculation point of the polyanion–polycation complex as the end point. Further suitable methods are a direct titration of the acid half-ester after ion-exchange of Na^+ against H^+ with a strong cation-exchanger, and a gravimetric determination of the sulfur content as $BaSO_4$ after cleaving the ester bonds, as well as glycosidic bonds, by boiling the sample in a mixture of HCl and $BaCl_2$ (Philipp et al., 1990). In our experience the

latter procedure is somewhat cumbersome but very reliable and gives as a result the total amount of sulfate, including that of inorganic sulfate present as an impurity, i.e. as Na_2SO_4. The latter can be determined separately by complexometric titration of the sample dissolved in a slightly acidic aqueous medium leaving the ester bonds intact. Figure 3.2.3 presents a comparison of results of the direct potentiometric titration with those of Schöniger combustion, followed by complexometric titration, and including also some results of ^{13}C NMR spectroscopic *DS* determination. The results of potentiometry and NMR spectroscopy coincide very well, while the S-content obtained by Schöniger combustion shows a rather large scatter, with some tendency toward negative deviations at low *DS*.

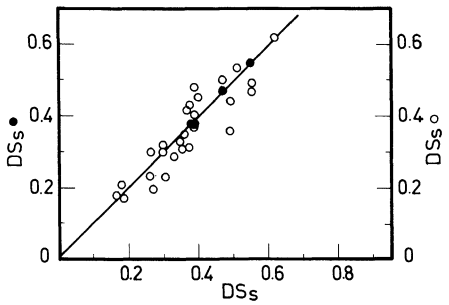


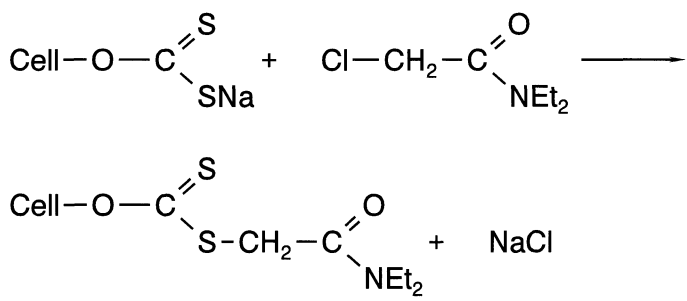
Figure 3.2.3. Comparison of three analytical techniques for determining *DS* of cellulose sulfuric acid half-ester, (○) complexometric titration after Schöniger combustion; (•) calculated from ^{13}C NMR spectra after enzymatic degradation versus DS_S obtained by potentiometric titration after cation exchange (Wagenknecht et al., 1991).

For the determination of nitrate groups a slightly modified Leclerq method (Leclerq and Mathé, 1951) was found to be convenient and reliable. It is based on a titration of the sample dissolved in concentrated H_2SO_4 with ferroammonium sulfate until the appearance of the slight brown color of the $Fe(NO)^{2+}$ complex formed with excess ferrous ions. Cellulose nitrite formed by dissolution of the polymer in the DMF/N_2O_4 system can be analyzed with regard to *DS* after precipitation with methylene chloride or acetone by dissolution in water and titration of the HNO_2 formed by ester hydrolysis with permanganate (Wagenknecht et al., 1977).

A special consideration is deserved by the xanthogenate group analysis in cellulose fiber xanthogenates, as well as in viscose spinning solutions, due to the industrial relevance of these intermediates in viscose fiber and filament production. The procedures practised today are based on the oxidation of the dithiocarbonic acid ester group by elemental iodine according to

$$2\ \text{Cell-O-CSS}^- + I_2 \rightarrow \text{Cell-O-CSS-SSC-O-Cell} + 2\ I^-$$

which, of course, requires the absence of other iodine-consuming sulfidic compounds like S^{2-} or CS_3^{2-} usually present in the viscose process. Fiber xanthogenates are, therefore, thoroughly washed with aqueous ammonium chloride solution or ethanol/water mixtures before analyzing the purified xanthogenate after redissolution in water. Viscose solutions can be depleted of low molecular sulfidic compounds after suitable dilution by passing through an anion-exchange resin, binding the low molecular sulfidic compounds only, but leaving the macromolecular cellulose xanthogenate unaffected. It is subsequently titrated in the aqueous solution as mentioned above. Also a decomposition of low molecular sulfidic compounds in a stream of CO_2 can be employed with advantage. A detailed procedure is given in the Appendix at the end of Vol. 1. Quite another approach for assessing the *DS* of cellulose xanthogenates consists of their conversion to a stable N-containing derivative by reaction with chloro-*N*,*N*-diethylacetamide according to the following scheme:



The next step consists of the determination of the nitrogen content of the isolated and purified reaction product (Philipp and Liu, 1959). For assessing the substituent distribution of xanthogenate groups within the AGU, the different rate of decomposition of C-6 xanthogenate on the one hand, and of C-2/C-3 xanthogenate on the other, to CS_2 and cellulose can be employed. The course of CS_2 liberation is monitored by transforming the escaping volatile product with a minimal time lag to ethylxanthogenate, or better diethyldithiocarbamate, by a spectrophotometric or polarographic technique, followed by kinetic data evaluation (Bär et al., 1966). These techniques played an important part some decades ago in the elucidation of xanthogenate group decomposition and xanthogenate group migration, but are today more favorably replaced by a ^{13}C NMR spectroscopic substitution-pattern analysis of the stabilized xanthogenate mentioned above.

3.3 Application of Spectroscopic Analysis in Cellulose Chemistry

In the analysis of cellulose and its derivatives instrumental methods are employed along two routes, i.e.
(i) for assessing the size and the chemical structure of the macromolecules within the entity of a given sample;
(ii) as a detection system for monitoring structurally relevant parameters during continuous fractionation of the polymer or chromatographic separation of its fragments.

The first of these routes will be the topic of this section, while the second one will be considered in the subsequent one dealing with fractionation and chromatographic separation. It has been emphasized already now, however, that along both routes of application of instrumental analysis adequate sample preparation plays a role.

Among the instrumental methods applied to structural analysis of cellulosic compounds, the spectroscopic techniques are dominating by far. In this subchapter some selected basic information on UV/visible-, IR- and NMR-spectroscopy are presented. The reader is referred for further details to subchapter 3.5, 3.6, Appendix Vol. 1 and to volume 2. These methods sometimes not only supply integral data over the whole sample, but also yield additional information on the distribution of chemical entities within the sample and, as in UV/visible and IR spectroscopy, they can additionally be employed to assess intermolecular interactions within the sample or between the polymer and the surrounding medium. Subsequently, some brief comments illustrated by examples mainly from our work will be given on the frequently used techniques of spectroscopy without going into details of a method.

Moving along the electromagnetic spectrum from the shortwave side, energy dispersive X-ray analysis has to be mentioned first as a relevant analytical tool at the borderline between spectroscopy and quantitative morphology, which permits the assessment of the integral concentration of elements heavier than carbon within the sample, as well as of the distribution of these elements on a sample surface or on a cross section of it. In the case of cellulosic materials, a principle limit is set to the accuracy of quantitative data by the surface roughness of the sample. Nevertheless, valuable semiquantitative information could be obtained by this method on the distribution of elements detrimental to chemical processing of cellulose fiber materials. This was shown by silicon distribution within the stalks of annual plants after various pulping treatments (Jacopian et al., 1980), and by metal cations like calcium in different fiber fractions of beech pulps (Bergner et al., 1990).

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A rather even SiO_2 distribution across the cell wall, with larger variation along the circumference of the circular cross section, can be concluded from these micrographs (Figure 3.3.1).

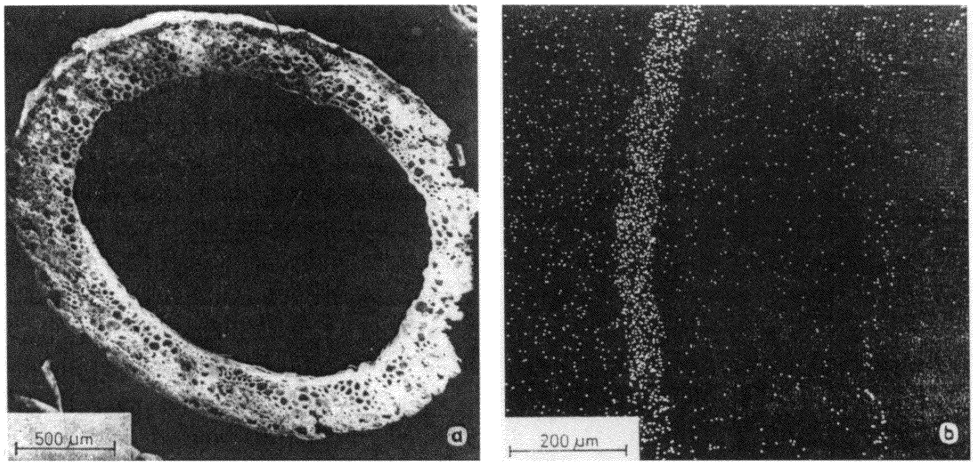

Figure 3.3.1. Visualization of SiO_2 distribution within the cross section of a wheat straw stalk: (a) reflection electron micrograph of the whole cross section; (b) SiO_2 distribution in a sector of cross section by energy dispersive X-ray point analyses.

Atomic absorption spectrometry is a standard routine method today for determining metallic elements down to the ppm range present as impurities in dissolving pulp or absorbed from the surrounding medium. The method requires an adequate sample preparation by dry or wet combustion to an injectable solution of the element in question. Examples of applications are the determination of the content of calcium in dissolving pulp (Zellcheming Merkblätter IV/56/76; IV/57/78) or the assessment of the binding capacity of cellulose xanthogenate for mercury ions from very dilute solutions (Schulze et al., 1983; Baumbach et al., 1985; Antow et al., 1996).

UV/visible absorption spectroscopy plays a rather marginal role in cellulose chemistry as most of the functional groups in question are inactive in the spectral region that is easily accessible to conventional equipment. Nevertheless, several routes of application have been successfully pursued for the determination of overall concentrations of chemical entities, as well as of their spatial distribution, and also for providing information on intermolecular interactions, as illustrated by the following examples. Dye absorption onto cellulosics, which is relevant in numerous processes of textile chemistry, as well as in carboxyl group determination by the methylene blue method (Appendix Vol. 1), can be assessed without problems by conventional UV/visible spectrometry. Aromatic substituents like the triphenylmethyl ether group usually show an absorption band in the

near-UV, and their concentration can be determined spectrophotometrically after dissolving the sample in a suitable, i.e. spectroscopically inactive, solvent. In a recent work the determination of the *DS* values of benzylcellulose samples was described after dissolution in Cadoxen by UV/visible spectrometry, arriving at a linear calibration curve in the *DS* range between 0 and 0.1 (Sollinger and Diamantoglou, 1996; see Figures 3.3.2 and 3.3.3).

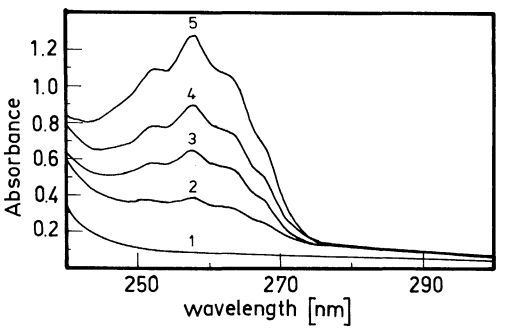

Figure 3.3.2. UV/visible spectrum of linters cellulose (1), and benzylcelluloses: *DS* = 0.021 (2), 0.048 (3), 0.071 (4), 0.110 (5) (Sollinger and Diamantoglou, 1996).

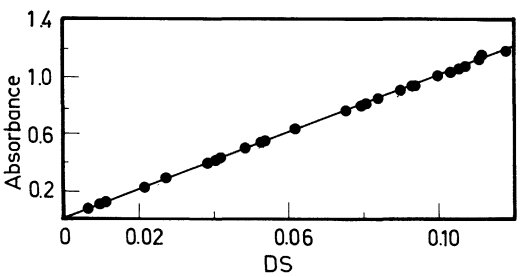

Figure 3.3.3. UV/visible calibration of the *DS* of benzylcellulose (Sollinger and Diamantoglou, 1996).

The UV/visible band of the C=O group in several dipolar aprotic liquids between 200 and 800 nm shows an absorption maximum for the $n\pi^*$ transition between 280 and 290 nm. The shift of this band was employed to investigate the formation of intermolecular hydrogen-bond complexes between dipolar aprotic liquids, as well as various polyhydroxy compounds, as model substances for cellulose (Berger et al., 1985). The equilibrium constants of complex formation and dissociation were assessed spectrophotometrically. The results were evaluated with regard to the mechanism of reaction of dipolar aprotic solvents like *N*-methylmorpholine-*N*-oxide or DMA/LiCl on cellulose.

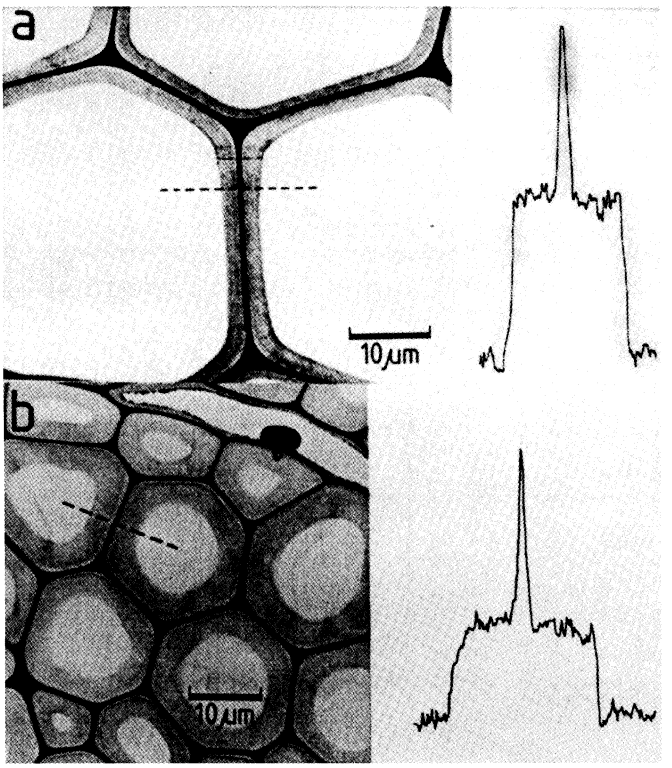

Figure 3.3.4. Ultraviolet micrographs of ultrathin sections (left) and the microdensitometer distribution curves (right) of lignin content across the cell wall measured along the dotted lines: (a) Spruce fibers; (b) Birch fibers (Fengel and Wegener, 1989).

The distribution of lignin as an aromatic constituent of wood and the change of distribution during pulping is known as a classical application of UV microscopy, which is still widely practised in pulping process. As an example, Fig. 3.3.4 presents the lignin distribution in the non-delignified fibers of two different wood species. The absorption maximum of lignin is situated at 270-280 nm, depending on wood species. (Fengel and Wegener, 1989).

Ample use is made today in cellulose research of IR spectroscopy in its various modes of performance. It can be applied to the qualitative identification of numerous functional groups in a macromolecule, via their IR-active bonds, and their quantitative determination in the concentration range above 1 %, employing either a polymer solution in a suitable solvent, a film of the polymer or a solid sample pressed to an opaque tablet in mixture with solid KBr. The solvents to be used must of course exhibit no IR signals within the spectral region in question.

Table 3.3.1. Functional groups of cellulosics Cell–OR susceptible to IR spectroscopy

Functional group R	Characteristic frequencies (cm^{-1})
$-CO-CH_3$	ν (C=O) 1755–1735
$-CH_2COOH$	ν (COOH) 1735–1705
$-CH_2COO^-$	ν_{as} (COO^-) 1640–1590
	ν_s (COO^-) 1425–1390
$-CH_2C_6H_5$ $-CH(C_6H_5)_2$ $-C(C_6H_5)_3$	ν (C–H_{arom}) 3100–3000 ν (C=C) 1610–1600; 1510–1490 δ (C–C) 705–700
$-Si(CH_3)_3$	δ_s (Si–CH_3) 1255—1250
	ν_{as} (Si–O–C) 1130–1120
	ν (Si–C), δ_r (CH_3) 840–829; 780–750
$-Si(CH_3)_2-C(CH_3)_2-C(CH_3)_2H$	δ_s (Si–C) 1253
	ν_{as} (Si–O–C) 1120–1115
	ν (Si–C), δ_r (CH_3) 835–830; 778
$-SO_2-C_6H_4-CH_3$	ν_{as} (>SO_2) 1370–1360
	ν_s (>SO_2) 1180–1175
	δ (C–H_{arom}) 814

Besides these classical modes of application, surface spectroscopy in the IR region is gaining importance also in the cellulose field, especially in the form of IR microscopy, supplying information additionally on the distribution of IR-active groups or compounds on the surface of e.g. a fiber, down to the μm range (Dechant, 1972; Kataoka and Kondo, 1996). Unfortunately, relevant data on the IR spectroscopy of cellulosics are rather scattered in the literature, and at the present state of knowledge the establishment of a data bank can be considered a real necessity. For a first orientation, some functional groups of cellulosics susceptible to IR spectroscopy are listed in Table 3.3.1. An example of functional group analysis by near-IR spectroscopy is presented by the spectra and the calibration curve, showing a high sensitivity even at $DS < 0.1$ for benzylcellulose (Sollinger and Diamantoglou, 1996).

Furthermore, IR spectroscopy is widely used today to obtain qualitative and quantitative information about the hydrogen-bond system of cellulose before and after chemical reactions via the different hydroxy bands concern. An overview of the IR bands of unmodified cellulose and the corresponding assignments taken from Gröbe (1989) is given in Table 3.3.2.

Infrared imaging with subsequent image processing has been recently employed for an in-situ investigation of the rate and uniformity of paper sheets (Kiiskinen et al., 1997).

Information obtainable from IR spectroscopy is efficiently supplemented today by application of Raman spectroscopy, as demonstrated by Sollinger and Diamantoglou (1996). Table 3.3.3 gives a comparison of *DS* data of benzylcelluloses obtained by UV/visible, near-IR and Raman spectroscopy. A still broader application of Raman spectroscopy in cellulose chemistry can be expected from further progress in instrumentation with regard to sensitivity and convenience.

A decisive role in the structural analysis of cellulose derivatives has been played for about 20 years high-resolution liquid NMR spectroscopy, especially with the ^{13}C and ^{1}H nuclei. A comprehensive review on the application of this spectroscopic technique in cellulose research has been published on ^{13}C NMR spectroscopy (Nehls et al., 1994). The ^{13}C NMR spectrum of unmodified cellulose consists of six signals, one for each of the six C atoms. The signals of C-1, C-4 and C-6 can be easily evaluated, while those of C-2, C-3 and C-5 sometimes pose problems of resolution due to their close proximity.

After complete reaction of the hydroxy groups (*DS* = 3), the spectrum in the region in question is still composed of six signals, exhibiting however a difference in chemical shift in comparison with unmodified cellulose, which is rather large at the C atoms directly involved, i.e. C-2, C-3 and C-6, but smaller at C-1, C-4 and C-5. After partial functionalization in all positions, principally two signals appear for each C atom, as shown in Fig. 3.3.5 for a partially substituted cellulose acetate with the two signals being completely resolved for the C-1 and C-6 positions.

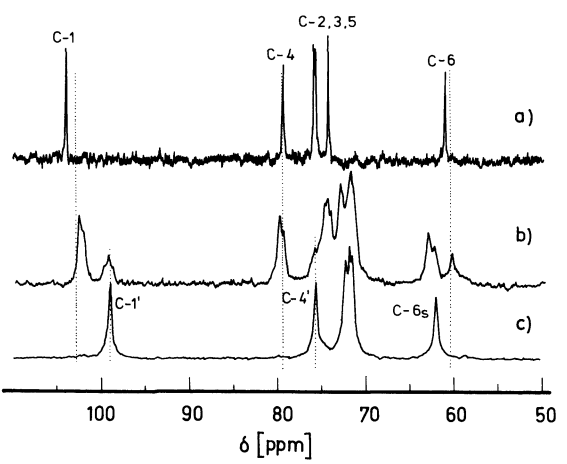

Figure 3.3.5. ^{13}C NMR spectrum of (a) cellulose; (b) cellulose acetate, *DS* = 1.50; (c) cellulose triacetate (index s means substituted, index ´ neighbour C-atom).

Table 3.3.2. Important IR-absorption bands of cellulose (Gröbe, 1989)

Position of absorption bands (in cm^{-1})				Assignment
Valonia, Bacterial cellulose	Cellulose I	Ramie, Cotton	Cellulose II	
		6770	6770	OH stretching, overtone
	5190		5190	absorbed H_2O, overtone
	4780		4780	OH and CH deformation + OH stretching
			4560	observed with cellophane only
	4365		4365	C–O stretching + OH stretching or CH_2 bending + CH_2 stretching
	4235		4235	OH and CH deformation + CH and CH_2 stretching
	3990		3970	C–O stretching + CH and CH2 stretching
	3125–3660			free OH and bonded OH stretching
			3484–3490	OH stretching of
			3444–3450	crystalline part of cellulose II after elimination of the amorphous part
	3200–3400		3200–3400	OH stretching, bands of H bonds
	3401–3405 ⊥			OH stretching
			3374–3394	OH stretching, maximum of absorption depending on origin of cellulose II
	3375			OH stretching
			3350–3360	broad band of OH stretching, obviously not resolved completely
3350 ∥		(3350) ∥		OH stretching
	3340–3345		(3340)	OH stretching
			3322	OH stretching
	3305 ⊥–3309 ⊥			OH stretching
		3300 ∥		OH stretching
	3275			OH stretching
3243–3245				OH stretching
			3163	OH stretching

Table 3.3.2. (cont.)

Position of absorption bands (in cm^{-1})				Assignment
Valonia, Bacterial cellulose	Cellulose I	Ramie, Cotton	Cellulose II	
	2970 ∥			CH stretching
		2967 ∥		antisym. CH_2 stretching
	2960			antisym. CH_2 stretching
	2945			antisym. CH_2 stretching
2914 ⊥		2910 ⊥		CH stretching
	2900		2900	broad band of CH stretching
2897 ⊥				CH stretching
		2880–2890		CH stretching
	2870 ⊥			CH stretching
	2853 ∥			sym. CH_2 stretching
	1760			C=O band from ester groups
	1730–1740			C=O stretching of carboxyl or lactone groups
	1635–1670			absorbed H_2O
	1550–1650			COO' stretching
	1590			COO' stretching
	1560			COO' stretching
	1530			COO' stretching
	1455 ⊥			OH in-plane bending
	1446 ⊥			OH in-plane bending, 'crystallinity band' (172)
	1440			OH in-plane bending
	1426–1430 ∥		(1426–1430 ∥)	CH_2 bending
	1380		1380	CH bending, same intensity with cellulose I and II
	1350–1450		1350–1450	COO' stretching
	1370		1370	COO' stretching
	1374 ∥			CH bending
	1370			CH bending
	1365			CH bending
	1350–1355		1355	
	1340		(1340)	OH in-plane bending
1336				OH in-plane bending

Table 3.3.2. (cont.)

Position of absorption bands (in cm^{-1})				Assignment
Valonia, Bacterial cellulose	Cellulose I	Ramie, Cotton	Cellulose II	
	1330–1335			OH in-plane bending
		1328		OH in-plane bending
	1320		(1320)	OH in-plane bending or CH bending
1317 ⊥				CH_2 wagging
	1315			CH_2 wagging
	1310			OH bending
	1290		1290	
1282		(1282 ∥) 1275 ⊥	1280	CH bending
	1250			
	1240		1240	
	1230–1235		1235	OH in-plane bending ?
	1210		1210	
	1205 ⊥		(1205)	OH in-plane bending
	1170		(1170)	
	1164		(1164)	stretching of C–O in ring or bending of C–OH
	1162 ∥			antisym. bridge oxygen stretching
	1125 ∥		(1125)	
	1120			antisym. in-phase ring wagging
	1119			C–O–C stretching
	1115		1115	'association band'
	1110		(1110)	antisym. in-phase ring stretching
	1060		~1065	OH bending
	1058 ∥			C–O stretching
1040				
	1035 ∥			C–O stretching
	1025			C–O stretching
	1015 ∥			C–O stretching
	(1005)		1005	
	1000 ∥			C–O stretching, or C–C stretching
	(985–990)		990	C–O stretching
			970	

Table 3.3.2. (cont.)

Position of absorption bands (in cm^{-1})				Assignment
Valonia, Bacterial cellulose	Cellulose I	Ramie, Cotton	Cellulose II	
	(900–910)		900	CH bending or CH2 stretching, 'amorphous band'
	(893–895 ∥)		895	antisym. out-of-phase stretching
	~800			ring breathing
	~700 ⊥			OH out-of plane bending
	663 ⊥			OH out-of-plane bending
	~740 ⊥			CH_2 rocking
	~650			OH out-of-plane bending
	620		620	
	560			
	520		525	
	500			
	450		460	
	430		425	

∥: parallel, ⊥: perpendicular

Table 3.3.3. Comparison of various spectroscopic methods of *DS* assessment of benzylcellulose (Sollinger and Diamantoglou, 1996)

Sample	$DS_{UV/visible}$	$DS_{near\text{-}IR}$	DS_{Raman}
1	0.0685	0.0681	0.0694
2	0.0678	0.0682	0.0655
3	0.0688	0.0689	0.0661
4	0.0693	0.0696	0.0712
5	0.0687	0.0700	0.0740
6	0.0682	0.0681	0.0734
7	0.0687	0.0687	0.0642
8	0.0683	0.0683	0.0774

According to these strongly simplified statements, the high-resolution liquid ^{13}C NMR spectrum of a cellulosic compound yields information on whether or not a reaction has taken place, to what extent a functionalization occurred on the different sites of the AGUs, and by addition of these partial *DS* values, on the

total *DS* of the sample. The calculation of partial *DS* values in the C-6 position of a cellulose acetate is shown schematically in Fig. 3.3.6.

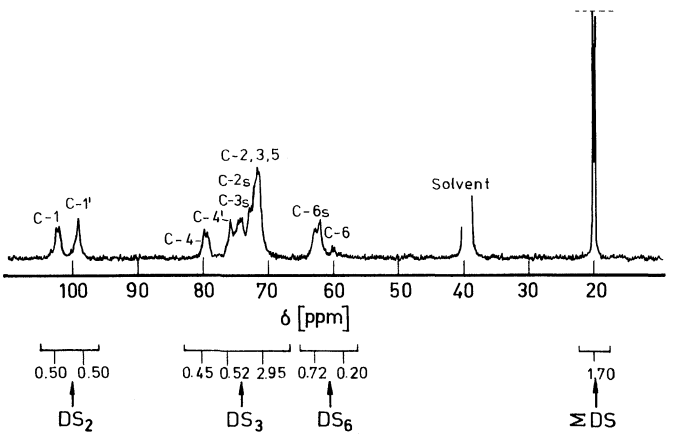

Figure 3.3.6. Scheme of calculation of partial *DS* values of cellulose acetate from the appropriate ^{13}C NMR signals.

The most important asset of the method is the fast and reliable information on the substituent distribution within the AGU. The chemical shift and the chemical shift difference to unmodified cellulose of ^{13}C NMR signals of some conventional cellulose derivatives is listed in Table 3.3.4.

Due regard, however, has to be given in practical use to some limitations of this technique:

(i) the sensitivity of the ^{13}C-NMR spectroscopy is rather low, in the region of 5 %. A polymer concentration of at least 5 % and preferably 10–20 % are required and an error in the determination of *DS* values of about 0.1 *DS* units has to be taken into account;

(ii) a high solution viscosity results in signal broadening and decreases signal resolution, especially in the C-2/C-3/C-5 region, requiring either the use of low-*DP* cellulose, e.g. level-off *DP* cellulose powders or a reduction in *DP* of the sample prior to NMR analysis by acid or enzymatic hydrolysis and ultrasonic degradation without splitting-off or transforming the substituents present;

(iii) even with high-quality NMR equipment and after adequate reduction of solution viscosity, difficulties can arise in resolving the signals in the C-2/C-3/C-5 region, impeding an accurate determination of partial *DS* at C-2 and C-3 separately. A satisfactory determination of the partial *DS* at C-2, however, can frequently be accomplished by evaluating the signal of the neighboring C-1 atom, which also exhibits a splitting into two signals with an area ratio proportional to that at C-2.

Table 3.3.4. ^{13}C NMR signal shifts of cellulose derivatives (Nehls et al., 1994)

Sample	*DS*	^{13}C NMR chemical shift (ppm)					
		C-1 / C-1'	C-2 / C-2_S	C-3 / C-3_S	C-4 / C-4'	C-5 / C-5'	C-6 / C-6_S
Cellulose	-	103.5-	74.6-	75.7-	79.8	76.4	61.3
Methylcellulose	3.0	-	-	-	-	-	-
		103.1	83.7	85.1	77.5	74.9	70.4
Ethylcellulose	3.0	-	-	-	-	-	-
		103.0	82.1	82.6	77.4	75.3	68.8
Propylcellulose	3.0	-	-	-	-	-	-
		102.6	82.2	83.8	77.2	76.7	68.7
Butylcellulose	3.0	-	-	-	-	-	-
		102.8	82.3	84.0	77.0	75.6	68.7
Cellulose formate	1.1	104.5	73.5	76.3	81.8	74.6	61.9
(in Me_2SO-d_6)		103.7	*	*	80.7		64.2
Cellulose acetate	2.0	104.4	73.1	76.5	81.6	74.7	61.0
(in Me_2SO-d_6)		101.1	*	*	80.3		63.9
Cellulose carbanilate	3.0	-	-	-	-	-	-
(in acetone-d_6)		101.7	74.1	74.6	78.1	73.1	63.8
Cellulose nitrate	2.8	-	-	-	-	-	-
(in Me_2SO-d_6)		99.0	79.2	77.9	76.3	70.6	70.6
Cellulose sulfate	1.3	103.0	73.2	74.7	79.2	73.6	60.8
(in D_2O)		100.9	80.4	82.4	78.4		67.1
Cellulose phosphate	0.3	104.1	75.4	76.7	78.7	76.5	61.7
(in Cadoxen)		102.7	*				63.9

A combination of ^{13}C and ^{1}H spectroscopy (two-dimensional NMR spectroscopy) has been successfully applied for a reliable signal assignment of the spectra of cellulose derivatives, e.g. cellulose nitrite (Wagenknecht et al., 1992). The measurements can be performed either with the original or with the degraded polymer in order to assess data on the partial degree of substitution at the different sites. Essential in any case is an adequate chemical modification of the polymer in order to achieve sufficient solubility in conventional solvents on the one hand and a satisfactory peak resolution in the NMR spectrum on the other. Using ^{1}H ^{1}H COSY NMR technique the distribution of functional of cellulose trialkylsilylethers has been investigated (Koschella and Klemm, 1997). Besides the high-resolution liquid ^{13}C NMR spectroscopy, solid state CP-MAS ^{13}C NMR spectroscopy is relevant to cellulose chemistry and physics, as will be discussed in connection with supramolecular order in a later section of this chapter. In solid, as well as in liquid, ^{13}C NMR spectroscopy an enrichment

with ^{13}C nuclei at specific positions of the AGU can be of advantage, as demonstrated in Fig. 3.3.7 for a bacterial cellulose, biochemically enriched with ^{13}C at the C-1 position (Evans et al., 1996).

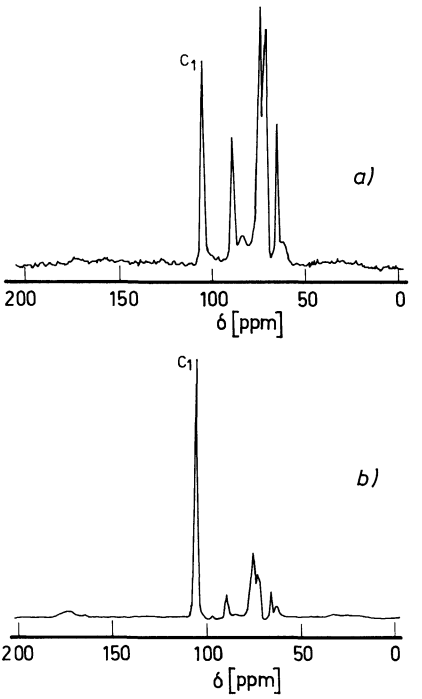

Figure 3.3.7. Solid state ^{13}C NMR spectra of bacterial cellulose (Evans et al., 1996): (a) conventional bacterial cellulose, (b) bacterial cellulose ^{13}C enriched in the C-1 position.

Furthermore, the NMR signals of some hetero nuclei, such as ^{7}Li (Morgenstern and Kammer, 1996), ^{29}Si (Schuldt et al., 1994) and ^{31}P, can yield additional information on the structure of cellulosic compounds or, as in the case of ^{7}Li, on the structure of intermolecular hydrogen-bond complexes formed between cellulose and components of the solvent DMA/LiCl. It is to be mentioned here that intermolecular interactions in these nonderivatizing solvents usually do not show up in the ^{13}C NMR spectrum (Nehls et al., 1994). Pertinent information on intermolecular interactions relevant to cellulose chemistry can sometimes be obtained from liquid NMR relaxation measurements, e.g. via the width of the ^{23}Na signal on hydrate formation in aqueous NaOH solutions (see chapter 4.2), or on the sorptive binding of NaCl on the one hand, or NaOH on the other, onto cellulose in aqueous suspension (Kunze et al., 1981).

Mass spectrometry as a method itself still plays a marginal role in cellulose analysis, but finds ample application in combination with chromatographic separation techniques (see the following section). The current rapid progress, however, in the area of mass spectrometry as a very powerful analytical tool may change this situation in the near future, as already oligomeric and low-DP polymeric polysaccharides have been efficiently analyzed by these technique due to its expansion to higher mass numbers of the fragments, up to 10^3. Up to now, results of mass spectrometry have played an important part in studies on the thermal decomposition of cellulose, as demonstrated by an example in Fig. 3.3.8 of the pyrolysis products of cellulose from *Acetobacter xylinum* at 540 °C.

The role of static and dynamic light scattering as an indispensable optical technique of general polymer analysis has already been considered in connection with molar mass determination of cellulosic compounds, and will be considered further in a subsequent section regarding the state of solution of cellulose and its derivatives.

In comparison with the impact of modern spectroscopic techniques on structural analysis of cellulosic compounds, other categories of instrumental analysis are of minor importance only. This holds true for electrochemical as well as for caloric methods. Potentiometry and to some extent also conductometry are employed in the conventional manner for characterizing ionic cellulose derivatives, for example with regard to pK values (Kötz et al., 1991), and their interaction with oppositely charged chemical entities, for example polyelectrolytes (Dautzenberg et al., 1994). Various polarographic techniques, i.e. the registration and evaluation of polarographic waves due to polymer adsorption on the dropping mercury electrode, have been employed by Reiche et al. (1978) to study the behavior of various cellulose derivatives differing in functional group and *DS* in these sorption processes.

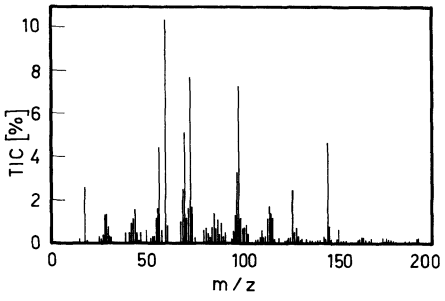

Figure 3.3.8. Average background-corrected mass spectrum of the pyrolysis products at 540 °C of cellulose from *Acetobacter xylinum* (Evans et al., 1996): TIC, Total Ion Current; m/z, mass to charge.

Techniques of thermoanalysis, like TG, TDG, DTA and DMTA (Hense-Wethkamp et al., 1995) have served so far mainly for the characterization of material properties of cellulosics. For instance, the thermal behavior of cellulose tosylates (Heinze et al., 1996) was studied. Recently TG measurements were also employed for testing the purity of thermally unstable cellulose derivatives (Liebert et al., 1994).

3.4 Techniques of Polymer Fractionation and Chromatographic Separation in Cellulose Analysis

This section on fractionation and chromatographic separation will be centered on advantages and limitations of the analytical techniques in practical application. Nevertheless, the following general remarks may be useful as an introduction.

From the viewpoint of physical chemistry, the techniques of fractionation and separation considered here can be traced back to the three principles of species-dependent solubility in a surrounding liquid, of species-dependent interaction with a sorbent, or of species-dependent transport velocity through a porous medium. Frequently more than one of these principles is effective in a procedure of separation. But usually one of them dominates by far, the first one e.g. in classical precipitation fractionation, the second one in the various modes of adsorption chromatography, and the third one in size-exclusion chromatography (SEC)/gel-permeation chromatography (GPC). Peculiar to cellulose and other polysaccharides is that these principles of separation can be realized with the polymer itself, as well as with its fragments obtained by hydrolysis or acetolysis or other modes of solvolysis of the glycosidic linkages. The oligomeric or monomeric fragments resemble adequately the chemical structure of the structural units along the original macromolecule. Regarding the practical procedure, the principles of separation can be realized by the stepwise preparation and analysis of fractions as in the classical fractionation of cellulose. This is possible by precipitation, or by cutting and investigating fractions from the effluent of a continuous separation in a column, or – as practised today in SEC and HPLC – by monitoring continuously relevant molecular parameters during a continuous column fractionation or separation. These general statements shall now be substantiated by considering various fractionation/separation techniques and their applicability to cellulose analysis, starting with fractionation techniques for cellulose and cellulose derivatives as polymers, and then turning to the separation and identification of fragments of cellulosics obtained by cleavage of the glycosidic bond.

Based on the principle of chain length dependent solubility of polymers, unmodified cellulose can be fractionated with regard to *DP* by preparing fractions

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either by extraction with a liquid of sufficient solvent power or by precipitation from a solution by stepwise addition of a nonsolvent. As compared with the stepwise fractionation by precipitation, extraction techniques are more convenient and time saving, but possess the inherent shortcoming that macromolecules to be dissolved according to their chain length may possibly remain in the residue due to incomplete accessibility of the solvent. Nevertheless, the latter techniques are still widely used in practise for a fast orientation, especially with respect to the content of short-chains. The most simple route is a subdivision of a dissolving pulp into a soluble and an insoluble fraction by extraction with aqueous sodium hydroxide of a given concentration, and subsequent determination of either the insoluble residue after adequate washing and drying, or of the amount extracted by wet combustion with $K_2Cr_2O_7/H_2SO_4$ and titration of excess reagent. By extraction with 10 or 18 % aqueous NaOH, the solubilities S_{10} and S_{18} or the residues R_{10} and R_{18} are obtained as information on the content of short-chain cellulose and hemicellulose, with $S_{10} > S_{18}$ and $R_{10} < R_{18}$, due to the dependency of solvent power on NaOH concentration (see chapters 2.1, 2.2 and 4.2, and detailed procedure in the Appendix at the end of Vol. 1). These S or R values now widely replace the older 'α cellulose determination' by extraction with 17.5 % and then with 8.0 % NaOH, giving values in between R_{10} and R_{18}. For a more detailed and precise characterization of this short-chain part of the pulp up to a *DP* of about 200, an extraction procedure has been described (Bergner et al., 1991) that employs aqueous NaOH solutions of increasing concentration containing Na-zincate for enhancing the ultimate solvent power, and a subsequent analysis of the cumulative fractions according to polymer concentration and specific viscosity.

A determination of the complete molar mass distribution curve of cellulose has been performed by precipitation-fractionation after conversion to the trinitrate or tricarbanilate employing an organic liquid, e.g. acetone, as solvent and water as the nonsolvent, and characterizing the fractions obtained by their mass and their intrinsic viscosity. The classical nitrate fractionation after full esterification of the hydroxy groups with minimal chain degradation, and dissolving the cellulose ester to a molecularly dispersed state, is still of interest as a reference method and is therefore described in detail in the Appendix at the end of Vol. 1. Starting from the nitration procedure with fuming nitric acid and P_2O_5 (Philipp and Linow, 1965), a fully automated SEC fractionation for cellulose nitrate according to *DP* was described by Fisher. An SEC column, with crosslinked polystyrene gel and tetrahydrofuran as the solvent for separation of the cellulose nitrate, was developed (Fischer et al., 1989). The effluent is continuously monitored by a refractive index detector for polymer concentration and by an automated viscometer unit for assessing $[\eta]$, and additionally by a light-scattering unit for controlling the $[\eta]$–M correlation. Good agreement of the results obtained with those of a cellulose tricarbanilate fractionation was observed, indi-

cating that nitration can be performed with just as little chain degradation as carbanilation, well-known for maintaining the original chain length.

Dissolution of various cellulose samples (wood pulp, cotton linters, viscose rayon) in the non-derivatizing solvent system DMA/LiCl with subsequent assessment of molar mass and of molar mass distribution by SEC with polystyrene standards was reported in (Silva and Laver, 1997), emphasizing the effect of molar mass and crystallinity on the conditions of dissolution required.

Fractionation of partially functionalized celluloses, for example cellulose acetates, with a *DS* between 1.8 and 2.5, or of Na-CMC, with a *DS* between 0.5 and 1.0, generally raises the problems of a superposition of separation according to *DP* and separation according to *DS*, although a strong preference for one of these parameters can sometimes be realized by suitable experimental conditions. Cellulose acetates obtained by dissolution acetylation can be fractionated in glacial acetic acid solution preferentially according to *DP* with *n*-heptane as the nonsolvent, preferentially according to *DS*, with water as the nonsolvent (Bischoff and Philipp, 1966). The fractionation of Na-CMC from aqueous solution poses additional problems, as precipitates of highly hydrated water-soluble cellulose ethers are generally hard to deswell, and as the gel content always present interferes with the 'normal' course of fractionation and rules out the use of a highly automated chromatographic technique. These problems have not been solved completely so far, although successful fractionation experiments have been reported, employing water, aqueous NaOH, or Cadoxen as solvents and electrolytes like NaCl or alcohols as precipitants. Ju Burevic and Nadzimutov (1976) describe a separation according to *DP* in the range from 50 to 5000, and Rinaudo (1969) reports a preferential separation according to *DP* or according to *DS* depending on experimental procedure, including variation in pH value of the medium. Remarkable progress in the analysis of cellulose xanthogenate as a technically important derivative was achieved without a stabilizing pretreatment of the polymer via a combined *DP* and *DS* fractionation by means of size-exclusion chromatography (Fischer et al., 1994). For a continuos multiple detection, a UV detector for monitoring xanthogenate group concentration, a light-scattering detector for indicating molar mass, and a refractive-index detector for measuring polymer concentration, were applied in series. According to this study, a poor filterability of viscose at sufficiently high CS_2 input, is mainly caused by too low *DS* of xanthogenate groups in the high molecular fraction of the polymer. This technically and economically important result clearly demonstrates the relevance of instrumental analysis for an efficient chemical processing of cellulose.

The characterization of the substitution pattern of partially derivatized products requires a tailored combination of steps of chain cleavage at the glycosidic bond, down to the oligomer or monomer level, with the appropriate techniques of chromatographic separation and fragment characterization. Eventually it includes also additional steps of derivatization, for example permethylation (see

chapter 4.5), or acetylation. These tailored combinations of chemical procedures and instrumental techniques led to remarkable progress in the assessment of substitution patterns within the AGU and also along the polymer chain. Derivatives predominantly studied so far are methyl-, hydroxyalkyl-, and carboxymethylcelluloses, as well as cellulose acetates.

For chain cleavage of cellulosics to oligomers or monomers, acid hydrolysis of the glycosidic bond, especially by H_2SO_4, $HClO_4$, and trifluoroacetic acid, is frequently used (see chapter 2.3). This technique works well with many cellulose ethers and of course unmodified cellulose (pulp), but often causes problems with cellulose esters due to partial saponification of the ester group in the acid medium. Alternatives reported are

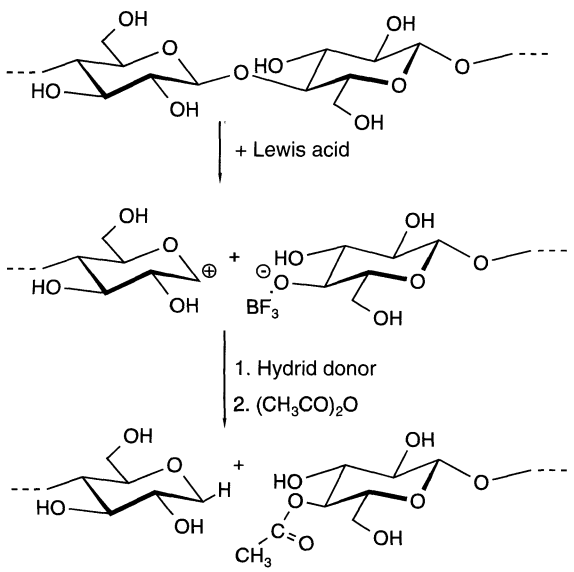
(i) methanolysis with H_2SO_4 or HCl as the acid;

(ii) solvolysis with liquid hydrogen fluoride (Jadav et al., 1994), resulting in glycosyl fluorides, which are subsequently hydrolyzed by water;

(iii) reductive cleavage to alditols, often combined with the subsequent acetylation to the corresponding alditol acetates for further separation;

(iv) enzymatic hydrolysis promoted today by the availability of well-defined cellulolytic enzymes and enzyme components (Saake et al., 1997), but often limited to samples of low to medium *DS*.

The so-called reductive cleavage is gaining in relevance in general polysaccharide chemistry and also in cellulose chemistry. It represents a special case of the ionic hydrogenation of carbonylic compounds according to Kursanov (Kursanov et al., 1974) and can be visualized for cellulose by the following simplified scheme:



Lewis acid:	Hydrid donor:
• $BF_3 \cdot OEt_2$	• Et_3SiH
• TMS-triflate	• $BH_3 \cdot SMe_2$
• TMS-triflate/$BF_3 \cdot OEt_2$	
• TMS-mesylate/$BF_3 \cdot OEt_2$	
• TMS-trifluoroacetate/$BF_3 \cdot OEt_2$	
• TMS-trichloroacetate/$BF_3 \cdot OEt_2$	

TMS, trimethylsilyl.

The subsequent acetylation of the alditols obtained has to be adapted to Lewis acid and reductant employed.

The completeness of degradation to the monomer level or the intended oligomer level can be controlled by GPC. In total, however, the step of chain degradation of partially functionalized celluloses needs further study and frequently a better adaptation to the type of sample in question, and thus still represents a challenge to cellulose chemists.

The separation of the fragments is generally performed via a species-dependent interaction with a stationary chromatographic phase. In the past, paper chromatography and thin layer chromatography were widely used to detect alien sugar residues in wood pulps after visualization of the sugar spots in the chromatogram by a suitable coloring procedure and subsequent photometric evaluation. Thin layer chromatography was frequently employed to assess the substituent distribution in cellulose ethers by photometric evaluation of the suitably visualized chromatographic bands of the different fragments. Today, predominantly high performance liquid chromatography (HPLC) or gas chromatography (GC) are used as time saving and effective routes for separating the fragments. The application of GC often requires a previous permethylation or persilylation of free hydroxy groups in order to secure adequate volatility of the fragments (Mischnick, 1995). For detection and identification of the fragments, GC is combined with mass spectrometry. As detector in HPLC, UV/visible and IR spectroscopic methods, conductometry, refractive index measurement and also mass spectrometry are used. The current development in this area is characterized by a trend toward multiple detection systems, higher-dimensional chromatography and the preparation and comprehensive analysis of defined oligomeric fragments.

These statements of a more general nature shall now be substantiated by some recently published examples. Heinrich and Mischnick (1996) determined the monomer composition of methylcelluloses after complete hydrolysis by means of ion-exchange chromatography for assessing the distribution along the chain. The samples were permethylated, introducing OCD_3 groups, partially degraded, and then investigated by fast atom bombardment mass spectrometry. An analo-

gous procedure was employed with cellulose acetates after permethylation and substitution of the acetyl groups by CD_3 groups. Arisz et al. (1995) assessed the substituent distribution of methylcelluloses along the poly mer chain by partial

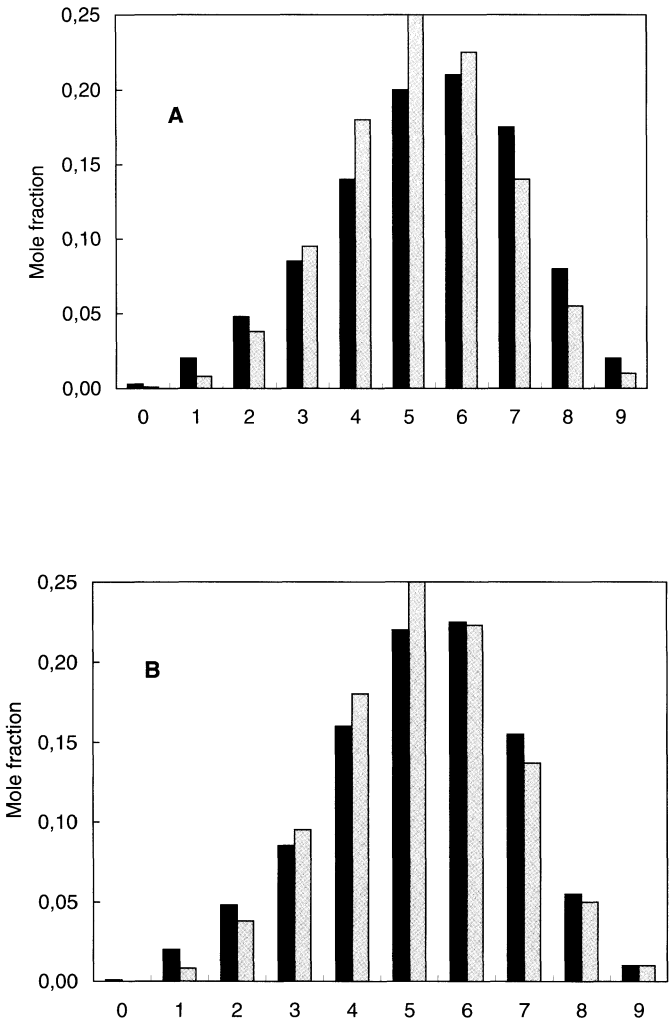


Figure 3.4.1. Comparison of the substitution pattern of triads of hydrolyzed methylcellulose (*DS* 1.75) determined experimentally (■) and calculated for a statistical distribution (□) (Arisz et al., 1995): (A) sample with large deviation from statistical distribution; (B) sample with small deviation from statistical distribution. Columns 1–9 denote the number of OCH_3 groups in each of the triad species.

hydrolysis to defined fragments and their subsequent fast atom bombardment mass spectrometry analysis after perdeuteriomethylation. The composition of the trimeric units investigated proved to be representative of the whole polymer chain and was compared with the calculated one on the basis of a statistical distribution. Significantly different deviations from the statistical distribution were observed between two samples of the same total *DS*, but prepared by different procedures of synthesis (Fig. 3.4.1).

The substitution pattern of carboxymethylcellulose along the polymer chain was studied by enzymatic degradation with purified endoglucanase, subsequent separation of the fragments by preparative GPC according to their chain length, followed by total hydrolysis of the fragments with dilute H_2SO_4 and a further separation of the hydrolysate components by anion-exchange chromatography employing amperometric detection (Saake et al., 1997). A synoptic evaluation of these results obtained by combining enzymatic and acid hydrolysis with analytical HPLC and preparative medium-pressure liquid chromatography can be considered as promising for data acquisition of substituent distribution along the CMC chains. A rapid and convenient procedure for determining the substitution pattern of CMC, has been developed (Liebert et al., 1996; Liebert and Heinze, 1997), employing a combination of complete acid hydrolysis, preferably with $HClO_4$, and HPLC.

The quantitative analysis of hydrolyzed CMC samples yields the mole fractions c_u (unmodified glucose), c_m (mono-*O*-carboxymethyl glucose), c_d (di-*O*-carboxymethyl glucose), and c_t (tri-*O*-carboxymethyl glucose). The average *DS* can be calculated:

$$DS_{HPLC} = c_m + 2c_d + 3c_t$$

The results obtained with 10 CMC samples (DS_{uranyl} range from 0.68 to 2.42) are graphically displayed as a function of DS_{HPLC} in Fig. 3.4.2. On the basis of a statistical model for the arrangement of substituents in cellulose derivatives – first proposed by Spurlin (1939) – the curves shown are calculated according to:

$$c_i = \binom{3}{k} (DS/3)^k (1 - DS/3)^{3-k}$$

where c_i are the mol fractions of unsubstituted, mono-, di-, and trisubstituted glucose units, k is the number of substituents per AGU (k = 0, 1, 2, 3) and *DS* is the average degree of substitution.

As demonstrated in Fig. 3.4.2, the determined values of the mole fractions are in good agreement with the statistical model. This means that the heterogeneous carboxymethylation is mainly determined by statistics. These findings agree well with the results of Reuben and Conner (1983), obtained by ^{13}C NMR spectroscopy of hydrolysates of CMC. The partial *DS* at the different positions within the AGU may be determined by means of ^1H NMR spectroscopy after hydrolytic chain degradation with D_2SO_4/D_2O (Baar et al., 1994; Liebert et al., 1996).

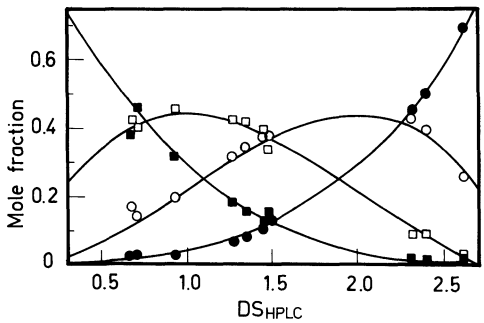


Figure 3.4.2. The mole fractions of ■, glucose; □, mono-*O*-carboxymethyl-, ○, di-*O*-carboxymethyl-, and ●, 2,3,6-tri-*O*-carboxymethyl glucose in hydrolyzed CMC samples, plotted as function of DS_{HPLC} (Heinze et al., 1994a).

3.5 Summary of Analytical Routes to Total *DS* and Substituent Distribution

As the degree of substitution (*DS*) and the pattern of substitution of a cellulose derivative can be considered the most important criteria in synthesizing new derivatives and developing new technologies for the chemical processing of cellulose, it seems appropriate to summarize in this brief section the present state of knowledge in this area. The total *DS* of cellulose derivatives can usually be determined by elemental or functional group analysis with a high accuracy. The routes frequently employed with important cellulose derivatives are summarized in Table 3.5.1.

Problems can arise, however, if
(i) the analysis is performed with a solid cellulosic and the full accessibility of the group in question cannot be *a priori* secured;
(ii) a partial sample decomposition cannot be completely excluded during purification, the determination of chemically bound NaOH in alkali cellulose being a classical example (see chapter 4.2);
(iii) the sample is liable to decomposition during analysis, as experienced with isolated cellulose trinitrite in the solid state.

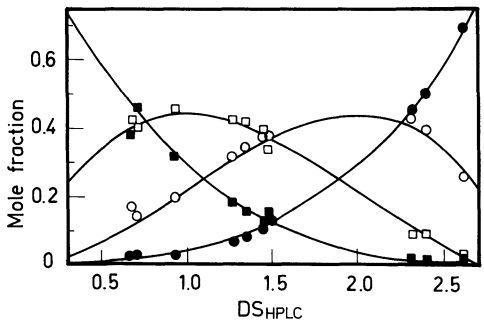


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Table 3.5.1. Survey of analytical techniques for the determination of total *DS* values of various classes of cellulose derivatives without subsequent modification.

Derivative	Analytical technique employed					
	Elemental analysis	Functional group chemical analysis	Spectroscopic analysis			Colloid titration (Symplex formation)
			UV/visible	IR (Raman)	^{13}C NMR	
Formate		+		+	+	
Acetate		+		+	+	
Higher aliphatic esters	+	+		+	+	
Tosylate	+			+		
Nitrate	+	+			+	
Nitrite	+	+			+	
Sulfate	+				+	+
Halodesoxycellulose	+					
Phosphate	+				(+)	
Alkyl ethers		+				
Hydroxyalkyl ethers		+			+	
Carboxymethylether	+	+			+	+
Carboxylcellulose		+				+
Benzylether			+	+	+	
Trialkylsilyl ether	+			+	+	
Tritylether	+		+			
Cationic ethers	+					+

The distribution of substituents within the AGU, characterized by partial *DS* values at C-2, C-3 and C-6, can be assessed now with many derivatives with an error of about 0.05 *DS* units by quantitative high-resolution liquid ^{13}C NMR, as well as ^{1}H NMR spectroscopy, with the chemically determined total *DS* acting as a good check for the validity of the summa of the spectroscopically determined partial *DS* values. Problems are posed again here by the instability of the sample prior to or during analysis and additionally by poor resolution of the C-2 and C-3 signal. Improved NMR characterization of high molecular weight

polymers and polyelectrolytes through the use of preliminary ultrasonic degradation was investigated (Kulicke et al., 1993). By separation of monomeric fragments by HPLC or GC after complete chain cleavage, the chromatographic techniques provide information on the relative amounts of non-, mono-, di- and tri-functionalized units, and also on the frequency of substitution in the different positions of the AGU. A further asset of the chromatographic route is the feasibility of analysis of insoluble polymer samples.

Despite remarkable progress in recent years, the assessment of substituent distribution along and between the polymer chains still represents a challenge to cellulose chemists. Earlier studies meeting with only limited success were based on a substituent-dependent polymer precipitation in the case of the distribution between chains (Bischoff and Philipp, 1966), and on a substituent-dependent chain cleavage in the case of the distribution along the chain. Results by the latter route were obtained by partial hydrolysis of stabilized cellulose xanthogenates (Philipp and Liu, 1959), or by enzymatic cleavage of CMC, with the final glucose yield at a given *DS* being enhanced in the case of a highly nonuniform carboxymethyl group distribution along the chain (Gelman, 1982; Kasulke et al., 1988). But, as demonstrated clearly by the examples in the previous section, decisive further progress can be expected, especially from a combination of controlled chain cleavage and appropriate chromatographic techniques including advanced detection systems (Mischnick and Kühn 1996).

3.6 Characterization of the Structure of Cellulosics in the Solid State

A quantitative description of the solid state structure of cellulosics on the supramolecular and morphological levels is of interest especially for two purposes, i.e.

(i) the evaluation of cellulose starting materials prior to dissolution or heterogeneous functionalization;

(ii) assessing and describing comprehensively the material properties of products obtained via chemical processes, especially of regenerated cellulose fibers and films.

In this section the most important methods employed for these purposes will be considered briefly with regard to the information supplied. Besides the routes for assessing supramolecular and morphological bulk structure, some techniques of cellulose surface characterization are mentioned.

The most important source of information on the supramolecular order of cellulose and its derivatives is still the wide-angle X-ray scattering (WAXS) pattern based on measuring the intensity of the scattered monochromatic X-ray

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The most important source of information on the supramolecular order of cellulose and its derivatives is still the wide-angle X-ray scattering (WAXS) pattern based on measuring the intensity of the scattered monochromatic X-ray

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radiation in dependence on diffraction angle, based on the well-known Bragg formula of X-ray reflection at the lattice plane of a crystal, according to Fig. 3.6.1.

$$FS + SG = n\lambda \qquad \sin\theta = \frac{FS}{d} = \frac{SG}{d}$$

$$FS = SG = d\sin\theta \qquad FS = SG = d\sin\theta \qquad n\lambda = 2d\sin\theta$$

n = order of reflection, λ = wavelength
θ = Bragg angle, d = lattice layer distance

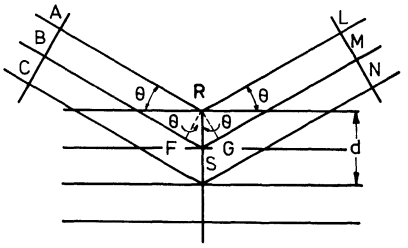


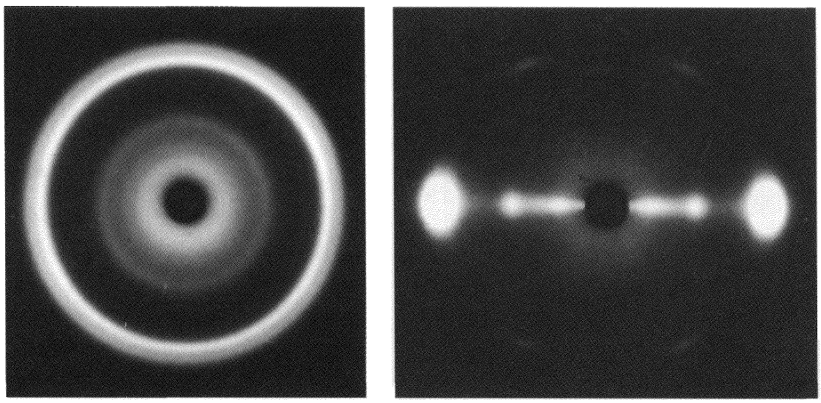
Figure 3.6.1. Derivation of the Bragg equation.

The following information can be obtained from the various modes of registration and evaluation of this diffraction pattern practised today (Fink and Walenta, 1994):
(i) crystal structure;
(ii) qualitative and quantitative phase analysis (lattice type and amount of mixed crystalline phases);
(iii) degree of crystallinity;
(iv) crystallite dimensions and lattice distortions;
(v) orientational state of crystallites (fibers and films);
(vi) short-range order of noncrystalline cellulosic materials.

Figure 3.6.2 illustrates this on an arbitrarily-chosen practical example of high and low oriented cellulose samples.

Data on (i) to (iv) can be assessed more or less completely also from the diffraction patterns of cellulose derivatives containing a sufficiently large percentage of X-ray crystalline material. The course of several heterogeneous reactions has been studied by taking wide-angle X-ray diagrams in dependence on a suitable reaction variable, e.g. the NaOH concentration in alkali-cellulose formation (see chapter 4.2). Furthermore, by combining a comprehensive evaluation of the X-ray pattern of highly crystalline cellulose samples with computer modeling, the positions of the atoms of the unit cell as the repeating units within the crys-

talline lattice could be determined, permitting conclusions on position and strength of intra- and intermolecular hydrogen bonds (Kolpak and Blackwell, 1976). On the other hand, a sophisticated evaluation of the X-ray scattering of non-crystalline cellulose samples yields information on short-range order concerning the conformation and the average distance of cellulose chain segments (Paakari et al., 1989; Ganster et al., 1994). Current methodical progress in wide-angle X-ray diffraction with respect to cellulose is characterized by an effective synergism of X-ray pattern evaluation and computer simulation on the one hand, and the combination of X-ray scattering with other methods like transmission electron microscopy (TEM), electron microspot diffraction, ^{13}C CP-MAS NMR spectroscopy on the other.



(a) (b)

Figure 3.6.2. Examples of WAXS pattern evaluation: (a) low orientation; (b) high orientation (Fink and Walenta, 1994).

Wide-angle X-ray scattering, as the most important technique to investigate the supramolecular order in cellulosics, is efficiently supplemented by several spectroscopic techniques: an NMR spectroscopic degree of order can be derived from the evaluation of the C-4 signal of the solid state ^{13}C NMR of cellulose, which is split into a very sharp crystalline peak and a broader amorphous peak due to the different electronic environments of this C atom in regions of high and low order as a consequence of different hydrogen-bond systems. This NMR spectroscopic degree of order can serve as independent information on supramolecular order, and is not directly proportional to X-ray crystallinity x_c (Unger et al., 1995). Figure 3.6.3 illustrates this by the NMR spectra of a highly ordered, medium ordered and low ordered cellulose I sample, showing clearly the decrease of the crystalline C-4 peak at 88–92 ppm and the increase of the corresponding 'amorphous' signal.

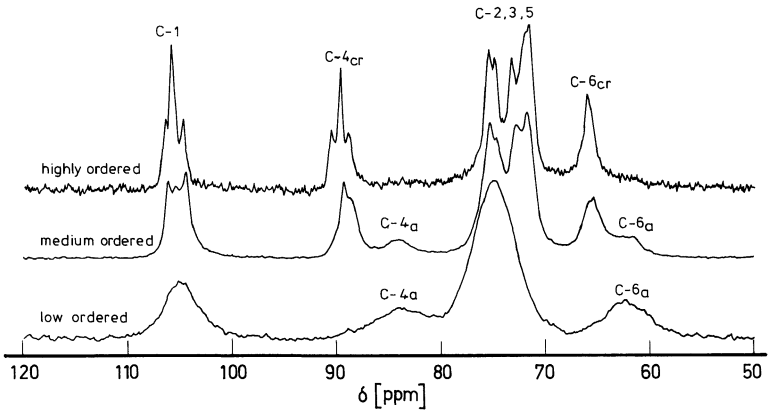


Figure 3.6.3. ^{13}C solid state NMR spectra of cellulose I samples (cr means crystalline, a amorphous) (spectra supplied by J. Kunze, Teltow-Seehof).

A similar inverse change of the peaks of 'crystalline' and 'amorphous' parts is observed in the C-1 and C-6 region of the spectrum. Furthermore, the signal shape at C-4 and also at C-1 permits the discrimination between the crystalline submodifications of I_α and I_β, with the valonia cellulose showing a high I_α content. A comprehensive discussion of the ^{13}C solid state NMR spectrum of cellulose with regard to the I_α and I_β submodifications has been given by Atalla and VanderHart (VanderHart and Atalla, 1984; 1987; Sugiyama et al., 1991). By special techniques of solid state MAS CP ^{13}C NMR spectroscopy quantitative information on supramolecular order and chain mobility was obtained from the C-1 and C-4 signals of Valonia, cotton and wood cellulose (Larsson et al., 1997). Also the FTIR spectrum in the region of the OH vibration band yields information on supramolecular order of the macromolecules (see Fig. 3.6.4), and it permits conclusions on the structure of the hydrogen-bond system in cellulosic solids.

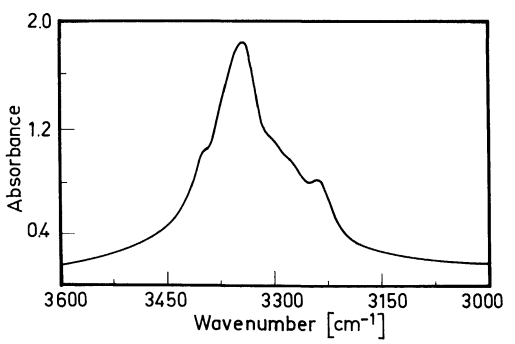


Figure 3.6.4. IR spectrum of valonia cellulose in the region of the OH stretching bands with the structuration of the signal being characteristic for a state of high order (spectrum supplied by A. Buchtemann, Teltow-Seehof).

Evans et al. (1995) compared X-ray crystallinity x_c with the IR spectroscopically determined crystallinity and the degree of order obtained by solid state ^{13}C NMR spectroscopy, employing pulp samples of decreasing lignin content. A close correlation between the three criteria was observed. For an explanation it is emphasized that x_c comprises a region of long-range order, while DO_{NMR} (degree of order by NMR) derived from the C-4 signal at 89 ppm (crystalline) and 84 ppm (disordered), is sensitive to short-range order. IR crystallinity was characterized in this study by the ratio of the absorption intensities at 1370 and 670 cm^{-1}.

The Raman spectrum of cellulose (Fig. 3.6.5) has also been successfully employed to gain a deeper insight into the supramolecular structure of the polymer.

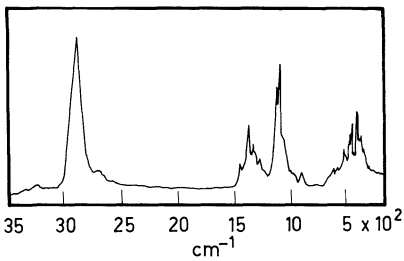


Figure 3.6.5. Raman shift of cotton cellulose (Xue, 1997).

Especially to be mentioned here is a microprobe technique (Wiley and Atalla, 1987), which permits the characterization of domains as small as 1 μm, and has been employed to study cellulose polymorphism and chain orientation. A combination of advanced techniques of WAXS, NMR, FTIR and Raman spectroscopy in studying cellulose supramolecular structure led to the important conclusion that the same heavy atom lattice can have more than one stable intermolecular hydrogen bond structure due to minor differences in chain conformation, and that this may explain differences in solubility of cellulose II obtained by mercerization on the one hand, and by regeneration from solution on the other (Isogai et al., 1987).

Besides the instrumental techniques considered above, numerous so-called accessibility methods have been used to gain information on cellulose supramolecular structure. Some of these methods, e.g. water regain, deuterium exchange, iodine sorption, or structure-dependent partial derivatization, have been mentioned already in previous chapters. As emphasized already, and as demonstrated again by the data in Table 3.6.1, the so-called ordered fraction of the structure differs widely depending on the methods employed, although more or less the same ranking of samples of widely different structure is observed.

Table 3.6.1. 'Ordered fraction' of some cellulose samples obtained by different methods (Bertoniere and Zeronian, 1987)

Technique	Cotton	Mercerized cotton	Wood pulp	Regenerated cellulose
Physical				
X-ray diffraction	0.73	0.51	0.60	0.35
Density	0.64	0.36	0.50	0.35
Chemical				
Acid hydrolysis	0.90	0.80	0.86	0.72
Formylation	0.79	0.65	0.69	0.37
Periodate oxidation	0.92	0.90	0.92	0.80
CMA [a]	0.73			
Sorption				
Deuteration	0.58	0.41	0.45	0.28
Moisture regain	0.58	0.38	0.51	0.23
Iodine sorption	0.87	0.68	0.73	0.48

[a] CMA = chemical microstructural analysis, based on availability of O(3)H.

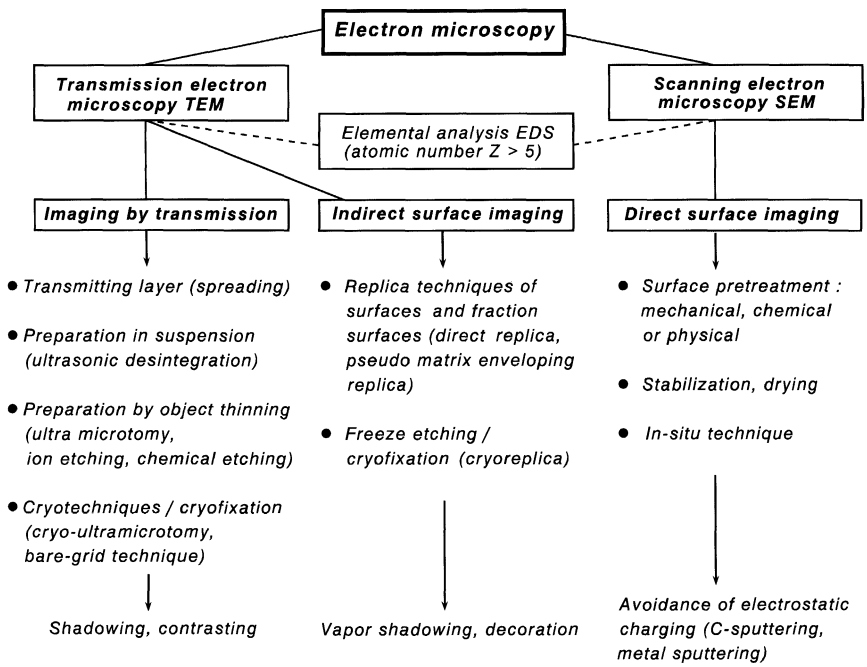


Figure 3.6.6. Techniques of sample preparation for electron microscopy (Purz et al., 1995)

The most important and versatile tool for investigating cellulose morphology is, of course, the electron microscope in the transmission (TEM) and the remetting scanning mode, in combination with a variety of highly developed preparation techniques for samples of different states of swelling (Purz et al., 1995, Fig. 3.6.6). A resolution down to about 0.3 nm in the TEM mode and about 1.5 nm in the reflection electron microscopy mode permits a detailed investigation of the ultrastructure of the fibrils, as well as of the void system in a broad variety of cellulosic specimens with minimal damage by the electron beam. In the μm range, electron microscopy is efficiently supplemented by modern developments in light microscopy, which can be combined today with automated image storage and computerized image evaluation. An appropriate scheme is presented in Fig. 3.6.7.

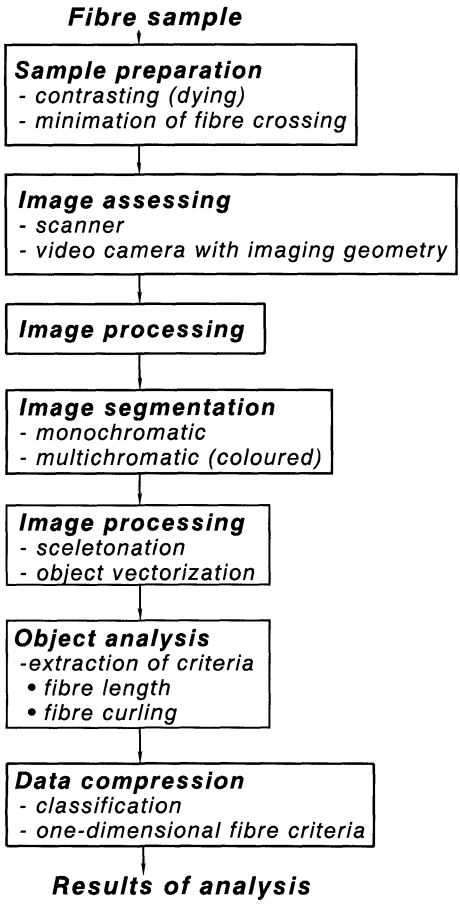


Figure 3.6.7. Scheme of determination of morphological fiber characterization by image analysis (Klein et al., 1996).

Cellulose-chemistry-relevant applications are the size-and-shape classification of cellulose particles (Unger, 1985) or the quantitative assessment of the fast initial state of cellulose fiber dissolution (Unger et al., 1995), or, as demonstrated earlier (Klare et al., 1959), the course of formation of a cellulose thread from a viscose solution.

Quite an other analytical approach to cellulose morphology is the registration and evaluation of the small-angle X-ray scattering (SAXS) pattern. Although less universal in applicability than electron microscopy, it yields some unique quantitative information on fibrillar and void morphology in the 1–100 nm range. As quantitative parameters characterizing the pore and void system of cellulosic specimens in the above-mentioned range, the overall void fraction of the sample volume and average void diameter, and the specific internal surface area of the void fraction may be mentioned here. On the other hand, fibrillar entities can be characterized with regard to lateral and especially also longitudinal periodicity (long periods), the detection of which, however, usually requires a previous degradation in the case of man-made cellulose fibers (Lenz et al., 1986). From the small-angle scattering data obtained, conclusions can be drawn with regard to fibril clustering and to the fractal dimensions of the morphological structure (Lenz et al., 1988). A fractal void structure was concluded due to clustering of cellulose microcrystallites from the decay of the SAXS curve, in contrast with a rather 'smooth' void boundary of valonia cellulose (Lin et al., 1987).

Analysis of pore size and shape by SAXS is supplemented and extended to larger pores by mercury porosimetry, which however is limited to pores available at the surface of the specimen, as only in these voids can mercury intrude under high pressure (Buschle-Diller et al., 1995). Figure 3.6.8 shows the pore-size distribution obtained by this technique for a bead cellulose before and after enzymatic treatment.

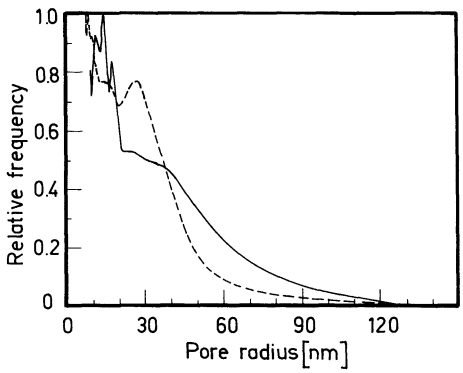


Figure 3.6.8. Pore-size distribution obtained by mercury intrusion in cellulose beads, untreated (---) and after 3 h of enzymatic hydrolysis (—) (Buschle-Diller et al., 1995).

Regarding the analytical characterization of the surface of a cellulose specimen, it must be emphasized again that the surface area of cellulose fibers and films is a frequently discussed but ill-defined quantity, the amount of which depends significantly on the yardstick used and on changes in this quantity during measurements due to swelling. The limits are represented by an outer surface derived from the geometry of this specimen as a minimum value, and the internal surface area derived from measurement of nitrogen or argon sorption in the dry nonswollen state via the Brunauer–Emmett–Teller sorption isotherm as a maximum value, including interfibrillar interstices and voids (see also chapter 2.1).

Sorption onto cellulose from the gaseous or liquid phase is usually studied either by depletion of sorbent in the ambient phase, for example in dye sorption, or by assessing the amount sorbed, for example in water vapor sorption via the increase in sample weight. Small amounts of tightly bound water can be favorably determined by Karl–Fischer titration.

For characterizing cellulose surface properties in textile or paper stock processing, e.g. after interaction with surfactants, the Zeta potential obtained by electrokinetic measurements is often employed as a criterion (Jacobasch et al., 1996).

In membrane application of cellulosics, the interface contact angle measured with water or an aqueous medium on the one hand, and with octane on the other, on a plane cellulose surface is a tentative criterion for the hydrophilicity/hydrophobicity ratio of the surface and thus for the interaction of the membrane surface with the substrate to be separated. For further details of the method and interpretation of results see Vienken et al. (1995).

Various topochemical techniques serve the purpose of assessing chemical entities (elements or groups) with regard to constitution and spatial distribution at the surface. The application of energy-dispersive X-ray analysis for the determination of heavier elements and of UV microscopy have already been considered in a previous section. Interesting results on the distribution of special groups in the cellulose moiety in recent years have been obtained by the use of FTIR microscopy, which shows a position sensitivity of 10×10 μm (Sollinger and Diamantoglou, 1996). Confocal Raman microscopy was quite recently recommended (Sollinger and Diamantoglou, 1996) for the visualization of functional group distribution on a cellulose membrane surface, as demonstrated in Fig. 3.6.9 for a benzyl group modified cellulose hemodialysis membrane.

Information on the structure of near-surface regions of a cellulose fiber or film can be obtained after depleting the specimen of its outer surface layer (or layers) by a so-called 'peeling procedure'. This can be accomplished by e.g. a surface acetylation and subsequent dissolution of the acetylated surface layer with an organic liquid, or by an enzyme treatment selective for defined structural entities. An example published recently is the removal of xylans from the surface of

kraft pulp fibers, followed by an 'electron spectroscopy for chemical analysis' of the 'new surface' formed (Buchert et al., 1996).

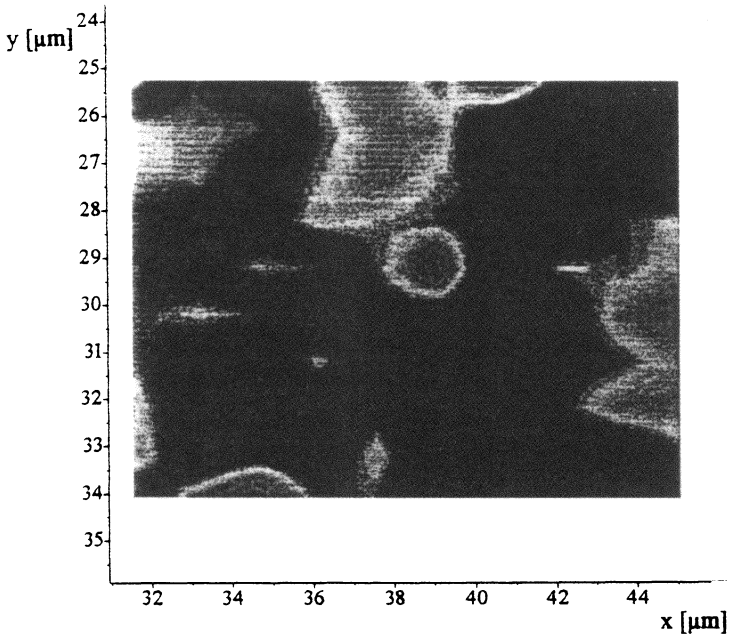


Figure 3.6.9. Lateral benzyl group distribution on the surfaces of a benzylcellulose dialysis membrane by confocal Raman microscopy (Sollinger and Diamantoglou, 1996).

3.7 Characterization of Cellulose-Liquid Interaction on Swelling and Dissolution

The limited swelling of cellulosic materials is usually characterized by the increase in weight or in volume (and thickness) of the sample due to uptake of liquid, employing samples in the form of films, pulp sheets, powdered materials or single fibers. The criterion of dominating relevance in practical work is the equilibrium swelling value, and also the rate of swelling, especially in the initial stages.

A frequently used technique is the determination of the so-called water retention value (WRV) of wood pulp or linters after a sufficient time of swelling in an aqueous suspension, subsequent centrifugation under defined conditions, followed by weighing of the sediment before and after drying (Jayme and Rothamel, 1948). The WRV is then calculated according to

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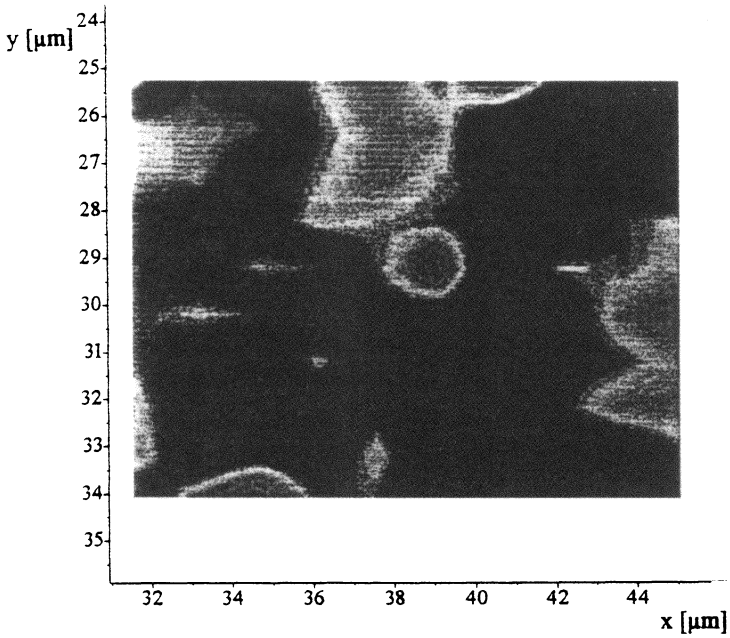

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$$WRV(\%) = \left(\frac{weight\ of\ sample\ in\ the\ wet\ state - weight\ of\ sample\ after\ drying}{weight\ of\ sample\ after\ drying} \right) \times 100$$

This procedure (see chapter 2.2 and Appendix of Vol. 1) can be adapted to assess limited swelling in other liquids and to particulate samples of different shape. In dependence on swelling liquid and particle shape, also the interstitial liquid between the particles contributes to the WRV to a varying extent (Philipp and Frommelt, 1980).

The viscose industry used the increase in thickness and/or weight of a pulp sheet in aqueous sodium hydroxide as the criterion of swelling on alkali-cellulose formation. The equilibrium value and the rate of swelling can also be determined via the uptake of liquid from a calibrated pipette (see Schwabe, 1954). Single fiber swelling is usually studied by measuring the increase in fiber thickness (fiber diameter) ten times along the fiber on different sides for a representative averaging. With slowly swelling liquids, e.g. DMSO in the case of viscose fibers, this procedure can be adapted to assess also the rate of swelling, while with fast-swelling liquid a videographic technique with subsequent computerized image evaluation can be recommended (Unger et al., 1995).

Increase in weight or volume on cellulose–liquid interaction cannot of course yield information on the mechanism of swelling. In combination with WAXS, for example, it allows to discern between intercrystalline and intracrystalline swelling. A quantitative and/or qualitative evaluation of light and electron microscopic images can serve to elucidate the mechanism of swelling at the morphological level (Unger et al., 1995). An interesting route to assess the spatial distribution of imbibed water in a sheet of pulp during drying by means of ^1H NMR imaging had already been mentioned in chapter 2.2.

A sophisticated techniques of NMR imaging ("Q-space imaging) was employed in (Li et al., 1997) to study water diffusion in porous cellulose fibres, discerning between "free" and "restricted" diffusion of the liquid.

The solubility of a cellulosic compound is frequently quite satisfactorily evaluated in the chemical laboratory by a visual classification according to 'soluble', 'partially soluble', and 'insoluble'. With partially soluble samples, a more or less quantitative separation into the soluble and the insoluble part can be performed by sedimentation or centrifugation. The data obtained, however, are not generally unambiguous, as small gels can remain in the supernatant, an optically clear liquid, and strongly sorbed soluble compounds can tightly adhere to the residue.

Information on the rate of dissolution can be obtained conventionally by separation into a soluble and an insoluble part, after suitable time intervals, although a registration of the decrease in turbidity with time of dissolution can be helpful in special cases under well-defined conditions of stirring. More

detailed information on rate and mechanism of dissolution of cellulose fiber and powder particles can be obtained by monitoring the number, size and shape of the particles during the process in a circulating suspension by means of a fast-responding optical cell according to Unger (1985). The optical system registers the light scattered by each single particle on passing a small orifice and converts the signals to data finally, characterizing particle length, cross sectional area of the particle in the flow direction, and its surface roughness. This technique of quantitatively evaluating a dissolution process via a 'reaction morphometry' has been applied so far to dissolution of cellulose fibers in FeTNa and in DMA/LiCl, but can be adapted to other problems of fiber swelling, fiber disintegration and fiber dissolution, too. Data evaluation in a three-dimensional diagram characterizing cellulose dissolution in DMA/LiCl is described by Berger et al. (1991).

The so-called state of solution of cellulose or cellulose derivatives dissolved in aqueous or nonaqueous systems has been frequently investigated and discussed in the recent decades due to its scientific and practical relevance, but still needs further systematic and methodical work for a really comprehensive characterization. Three main routes have been pursued up to now, i.e.

(i) the macromolecular characterization of cellulosic compounds after dissolution of the polymer to the level of molecular dispersion;

(ii) the quantitative assessment of deviations from this molecularly dispersed state of solution, including larger inhomogeneities, especially gel particles of different size;

(iii) the thorough rheological characterization of cellulosic polymer solvent systems, including an interpretation of results with regard to intermolecular interactions.

The first route is based predominantly on light scattering techniques and viscosimetry in very dilute solution at a polymer concentration usually below 0.1 %. Also sedimentation and rheo-optical measurements can be employed with advantage. Tentative information obtained concerns the intensity of solvent–solute interaction, on the one hand, and the shape of the macromolecules in solution, i.e. their state of coiling or their chain stiffness, on the other, with the so-called 'persistence length' as the most important quantitative parameter (Vollmert, 1962). Systems thoroughly investigated are e.g. cellulose trinitrate in acetone or carboxymethylcellulose in Cadoxen.

Most of the work published so far along the second route concerns cellulose xanthogenate solutions at different levels of concentration. The main reason for this is the practical relevance of inhomogeneities in viscose spinning solutions. Generally, inhomogeneities in solutions of cellulosic compounds can comprise the broad spectrum from aggregates of a few macromolecules to visible gels and fiber fragments. They can originate from residual supramolecular structures of the starting polymer or from secondary aggregation. It is therefore plausible that

this wide spectrum of inhomogeneities varying in size, shape, packing density and deformability cannot be reliably characterized by one single method, and that even a sophisticated combination of modern techniques up to now could not solve all the problems encountered in assessing quantitatively and unambiguously this particle spectrum. Filtration, optical and conductometric particle counting, turbidimetry, light scattering and rheometry are the techniques employed today as a single method or in combination with others.

To evaluate the quality of a spinning solution with regard to particle content, the determination of a clogging value is still most widely used. It is obtained at a standardized filtration test, measuring either the decrease in flow rate at constant pressure or the increase in pressure at constant flow rate. This is demonstrated below for the determination of a viscosity-corrected k_w or k_v value for viscose spinning solutions (Philipp and Schleicher, 1964).

Clogging value k_w:

$$k_w = 10^5 \times \frac{2 - b/a}{a + b}$$

Viscosity and filter-corrected clogging value k_v:

$$k_v = \frac{A \times k_w}{\eta^{0.4}}$$

a = filtrate (g) in the filtration time interval from 0 to 20 min
b = filtrate (g) in the filtration interval from 20 to 60 min
A = filter area (cm^2)
η = falling ball viscosity (s)

A high k_w or k_v represents a low viscose quality due to fast clogging of the filter by gel particles.

Optical and conductometric particle analyzers have the advantages of fastness, convenience and wide applicability in supplying data on particle size and size distribution down to the μm range of the particle spectrum. But the results are often somewhat ambiguous, as the signal of an optical particle-size analyzer depends on particle size as well as the optical density of the particle. The signal of a conductometric analyzer, based on the conductance decrease on passage of a particle through an orifice, is determined by the particle size, as well as its intrinsic conductance (Schleicher, 1964). Both techniques have been widely applied for several decades to viscose spinning solutions and have also been studied comprehensively with regard to their limitations. Moreover, the conductometric technique has been successfully employed to study thermal crosslinking of cellulose (Philipp and Stöhr, 1973), and insoluble impurities in cellulose fibers (Arnold et al., 1971), after dissolving the polymer in a metal-complex solvent of high solvent power. Comprehensive information at the small size end of

the particle spectrum, up to particle dimensions of some hundred nanometers, can be obtained from static and dynamic light scattering measurements. By a thorough evaluation of the data obtained, deviations from a molecularly dispersed state of solution can be detected, and aggregations of macromolecules persisting in the solution can often be quantitatively described, as shown by Burchard for various cellulose solvent systems (Seger et al., 1996), for dilute solutions of cellulose xanthogenate (Fischer et al., 1996).

Even a brief abridgement of the techniques of polymer rheology would by far surpass the scope of this book, and the reader must be referred to relevant literature, e.g. by Schurz (1974). Only two routes of general interest to the cellulose chemist will be mentioned briefly here.

(i) Comprehensive rheological investigation of cellulosic systems at higher concentration in dependence on shear rate, shear history, concentration and temperature, and often including a determination of the viscoelastic properties of the system. Usually couette or cone-plate viscometers are employed for this purpose. Special devices have been developed for assessing the so-called longitudinal viscosity of cellulosic spinning dopes as an important parameter in the spinning process (Schramm, 1995).

(ii) Application-oriented rheological measurements with solutions of higher concentration usually by a standardized procedure. Procedures of this kind are often practised with solutions of e.g. cellulose acetate, cellulose nitrate, cellulose xanthogenate or carboxymethylcellulose as cellulose derivatives of commercial relevance. The rheology of cellulose solutions is still a prospering area of scientific research and practical applications e.g. in cellulose processing, taking advantage of progress in instrumentation and computerized data evaluation.

3.8 Outlook for the Future Development of Cellulose Analysis

Current trends in general polymer analysis, relevant also to cellulose chemistry, are the combination of different methods in order to elucidate structures of increasing complexity, a tendency to assess distribution patterns of analytical parameters instead of average values, and a rapid progress in automation and computerization of analytical procedures.

Of special interest for cellulose chemistry in the near future are analytical developments along the following routes:

(i) advanced procedures for controlled degradation of cellulose and cellulose derivatives in order to obtain oligomeric sequences of defined length for subsequent analysis;

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(ii) tailored combinations of chromatographic techniques including detection systems, for example in multidetection systems and two-dimensional chromatography for a fast and reliable simultaneous determination of *DP* and *DS* distribution in cellulose derivatives;
(iii) elaboration of methods for a reliable quantitative assessment of very low *DS* values of functional groups;
(iv) further development of two-dimensional high-resolution liquid NMR spectroscopy tailored to requirements of cellulose chemistry, including also heteronuclei like ^{29}Si or ^{31}P;
(v) cellulose-adapted application of mass spectrometry in its different modes within the framework of polysaccharide analysis;
(vi) development of instrumentation and techniques in the area of topochemical analysis of quantitative, computerized image evaluation and light, electron, and atomic force microscopy, tailored toward the characterization of cellulosics in the solid state.

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Appendix to Volume 1:

Experimental Protocols for the Analysis of Cellulose

Comprehensive Cellulose Chemistry; Volume 1: Fundamentals and Analytical Methods
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Successive chain-length fractionation of cellulose nitrate from wood-pulp-regenerated alkali cellulose or viscose rayon

Preparation of the nitration acid

To 40 ml of 84 % by weight H_3PO_4 (ρ = 1.7 g/ml), 76 g of P_2O_5 are added in small portions, shaking the mixture vigorously before adding the next portion. After the acid mixture has been cooled down during 3–4 h with occasional shaking, 61 ml of white fuming nitric acid (ρ = 1.52 g/ml) are added in one portion, and this mixture is shaken vigorously. For storage times exceeding 24 h, the acid mixture should be kept at about 0 °C.

Sample preparation for cellulose nitrate synthesis

The dry sample is disintegrated in a suitable apparatus, e.g. an attrition mill, after previously cutting pulp samples to pieces of 5 mm × 5 mm, and filament samples to about 3 mm length. The disintegrated sample is dried for 2 h at 50 °C.

Preparation of the cellulose nitrate

A sample of about 0.8 g cellulose is mixed with 40 ml of the nitration acid, and cooled down to 0 °C. This mixture is shaken vigorously and then kept for 3 h at 0 °C with occasional shaking. Subsequently most of the nitrating acid is separated from the cellulose nitrate on a coarse sintered-glass crucible by pressing with a glass stopper. After putting the filter crucible onto a suction flask, the sample is neutralized stepwise by addition of a total volume of 240 ml of 2 % by weight aqueous Na_2CO_3 solution, which is filtered through the crucible without suction. Subsequently the sample is washed with about 8 l of distilled water, again applying no suction. After these washings, most of the water covering the sample is drawn off by suction, and the cellulose nitrate is stabilized for 2 h at room temperature by covering it with methanol in a beaker. After separating the methanol by filtration, the sample is dried *in vacuo* over P_2O_5 at 20 °C for at least 15 h.

Determination of the N-content of the nitrated sample (Timell and Purves, 1951)

A sample of about 100 mg of cellulose nitrate is weighed to the nearest 0.1 mg and then mixed in a 100 ml ground-glass Kjeldahl flask, with 400 mg of salicylic acid and 10 ml of concentrated sulfuric acid. With occasional swirling the sample is dissolved within 1–2 h. Samples of very high *DP* may require a somewhat longer time to dissolve. To the clear solution 1 g of Na_2SO_3 and 2 g of K_2SO_4 are added. The mixture is gently warmed up for about half an hour, and then heated for 2–4 h until the dark-colored solution is again quite clear.

After cooling the mixture to room temperature, 10 ml of H_2O_{dist} are added. Determination of the nitrogen present now as ammonium ion is performed in a Kjeldahl distillation apparatus by adding 20 ml of a 35 % by weight aqueous NaOH solution, and the NH_3 distilled off is bound in 10 ml of 0.1 N H_2SO_4. The excess of H_2SO_4 is back-titrated with 0.1 N aqueous NaOH using a Tashiro indicator (50 ml aqueous 0.1 % methylene blue solution + 100 ml 0.3 % by weight ethanolic methyl red solution).

Calculation

$$\% N = \frac{(ml\ 0.1\ N\ H_2SO_4 - ml\ 0.1\ N\ NaOH) \times 0.0014 \times 100}{g\ weight\ of\ sample}$$

The nitrogen content of the nitrated sample should amount to at least 13.6 %.

Fractionation

For one fractionation series, 300–350 mg of the cellulose nitrate are dissolved in an acetone/water mixture (95:5 % by volume) to give a solution containing 0.3 % by weight of cellulose nitrate. Before fractionation, the solution is filtered through a coarse glass-filter crucible for removing coarse impurities present. The fractions are precipitated by dropwise addition of the appropriate acetone/water mixtures from a burette. With high *DP* samples, the first fractions are precipitated by an acetone/water mixture, 3 : 1 by volume, and for the 3 : 5 fraction a 1 : 1 mixture is used for separating all the further fractions. For samples in the lower *DP* range (below about *DP* = 500) exclusively the 1 : 1 mixture is employed. The last but one fraction is precipitated with distilled water, and the last fraction is obtained by adding saturated aqueous NaCl solution. On adding the precipitants, the system should be vigorously shaken in order to avoid a clotting of the precipitate. Precipitant addition is stopped as soon as the first haze of a precipitate appears. In the case of high molecular weight samples the system is kept 1 h at room temperature subsequent to separation of the fractions No. 1, 2 and 3 in order to secure an equilibrium between the gel phase and the sol phase. In order to keep the first fraction small enough, it is recommended, at least with high molecular weight samples, to add pure acetone after the first haze has appeared until it is dissolved again. During the subsequent equilibration a precipitate separates again in an amount sufficient to obtain a first fraction.

For separating the precipitate of each fraction the system is centrifuged in closed 100 ml centrifuge beakers in a conventional laboratory centrifuge for 10 min at 3000 r.p.m. The clear solution is decanted back to the Erlenmeyer flask for the next step of precipitation. The centrifuged beakers are kept in a horizontal position, and after some drying in the open air are transferred in a weighed 100 ml brown glass bottle with ground glass stopper. The first three

fractions are dried *in vacuo* over P_2O_5, and all the following ones at maximal 50 °C in an oven for 2–3 h. After weighing, the mass of the fraction is obtained by difference. Usually 10–12 fractions can be obtained in this way.

Viscosity measurements

Depending on the *DP* to be expected, 30–100 ml freshly distilled acetone are added to each of the fractions, and the samples are shaken vigorously until a clear solution is obtained. Usually 1–5 h are required for this procedure. The solutions can be kept overnight at room temperature without impeding the *DP* measurements. The viscometer efflux time of the solution should not be more than three times the efflux time of the solvent; otherwise a further dilution is recommended. For determining the viscosity of the known fractionated cellulose nitrate a 30–50 mg sample is dissolved in the same way as described for the fractions.

For the viscometric measurements, Ubbelohde viscometers with a 0^a capillary are recommended. The measurements are performed at 20±0.05 °C. The efflux times are corrected according to Hagenbach (see Table 1). The efflux time of the pure solvent required for the subsequent calculations amounts to 80–90 s with the capillary 0^a.

From the Hagenbach-corrected efflux time t_1 of the solution and t_0 of the pure solvent the specific viscosity η_{spec} is calculated according to

$$\eta_{spec} = \frac{t_1 - t_0}{t_0} = \eta_{red} - 1$$

and the reduced viscosity is obtained according to

$$\eta_{red} = \frac{\eta_{spec}}{c}$$

with c being the polymer concentration in g/ml in the solution. For determining the limiting viscosity z_η the reduced viscosity is extrapolated by calculation according to

$$z_\eta = \lim_{c \to 0} \frac{\eta_{spec}}{c} = \frac{\eta_{spec}}{c} \times \frac{1}{1 + k_\eta \times \eta_{spec}}$$

with $k_\eta = 0.30$.

From z_η (ml/g) the *DP* is obtained according to

$$z_\eta = K_m \times DP$$

with $K_m = 0.73$.

Table 1 Hagenbach correction for Ubbelohde viscometer

Efflux time (s)	Correction (s)
70	4.30
80	3.76
90	3.34
100	3.01
120	2.51
140	2.15
160	1.88
180	1.67
200	1.50
250	1.20
300	1.00

For a polymer concentration of $c = 10^{-3}$ g/ml the *DP* value in dependence on specific viscosity can taken from Table 2.

From the mass and the *DP* of the fractions an integral and a differential molar mass distribution curve can be obtained along the conventional route (see Philipp and Linow, 1965).

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Table 2 Calculation of *DP* values in dependence on η_{spec}

η_{spec}	+ 0.00	+ 0.01	+ 0.02	+ 0.03	+ 0.04	+ 0.05	+ 0.06	+ 0.07	+ 0.08	+ 0.09
0.1	132	145	158	171	183	196	209	221	233	247
0.2	258	270	282	294	306	318	330	342	353	365
0.3	376	387	400	411	421	433	445	456	466	477
0.4	488	499	510	521	533	544	554	565	576	585
0.5	595	606	616	626	636	647	657	667	677	687
0.6	697	707	717	726	736	745	756	765	775	784
0.7	794	803	812	822	831	840	850	859	868	877
0.8	886	895	903	912	921	930	939	948	956	965
0.9	973	982	990	999	1007	1016	1024	1033	1041	1049
1.0	1057	1065	1073	1082	1090	1098	1106	1114	1123	1130
1.1	1138	1145	1153	1161	1168	1176	1184	1191	1199	1206
1.2	1214	1221	1229	1236	1244	1251	1259	1266	1273	1281
1.3	1288	1295	1302	1309	1316	1323	1331	1337	1344	1352
1.4	1359	1365	1372	1378	1385	1393	1399	1406	1412	1419
1.5	1425	1432	1439	1445	1451	1458	1465	1472	1478	1485
1.6	1491	1497	1503	1509	1515	1522	1528	1535	1541	1547

Preparation of level-off *DP* (LODP) cellulose by acid hydrolysis

70 g of air dry cotton linters or wood pulp are suspended in 1.5 l of aqueous 5 % by weight HCl, heated under reflux and gentle stirring to boiling during 30 min, then kept at boiling temperature for 30 min and then cooled down to room temperature in a further 30 min. The degraded cellulose is filtered off in a coarse sintered-glass-filter crucible and washed with distilled water free of acid. For removing the last traces of acid, an aqueous suspension of the degraded cellulose is neutralized to pH 8 with aqueous ammonia, filtered off again, washed with water and dried at 50 °C. The product yield is usually at a level of 90 %. The LODP observed depends strongly on the starting material and is about 160 for cotton linters and 180–220 for wood pulp, while with regenerated cellulose fibers or films, LODP values of between 30 and 50 were observed.

Reference

Loth, F., *Ph.D. Thesis Academy of Sciences (GDR)* **1975**.

Laboratory procedure for the preparation of decrystallized cellulose with liquid NH_3

10 g of cotton linters or dissolving pulp are predried at 105 °C for 15 h and then cooled down to –60 to –80 °C in a round-bottom flask equipped with a stirrer under exclusion of moisture. Liquid ammonia, condensed from NH_3 gas and cooled down to at least –60 °C, is added to the cellulose under stirring, to a solid to liquid ratio of 1:10 until 1:15. The mixture is kept stirred at –60 °C for 2 h. Then the temperature is raised to –33 to –30 °C, and the ammonia is distilled off and recondensed for further use. Then the temperature is slowly raised further over 2–4 h to ca. 20 °C and the last traces of NH_3 are eliminated by treatment under vacuum at that temperature with strict exclusion of moisture. The sample obtained by this procedure exhibits a very small decrease in *DP* only, and a WAXS diagram corresponding to that of a completely amorphous cellulose.

Reference

Procedure of the Fraunhofer Institute of Applied Polymer Research, Teltow-Seehof.

Preparation of a cellulose tricarbanilate

162 mg (1 mmol) of dry cellulose are shaken for 2 h with 15 ml of dry pyridine in an Erlenmeyer flask at room temperature for removal of water, and filtered off on a sintered-glass disk. The sample is then swollen again in 30 ml of dry pyridine under shaking overnight at room temperature. Then the sample is again filtered off and transferred to an Erlenmeyer flask with 6 ml of phenylisocyanate. The subsequent carbanilation is performed during 18 h at 90 °C under continuous shaking. After cooling to room temperature, 2 ml of methanol are added for decomposing residual phenylisocyanate. Then the reaction mixture is poured into 150 ml of an acidified methanol/water solution (methanol/water = 70 : 30 by volume with 50 ml of glacial acetic acid added per l). The polymer is filtered off on a hard paper filter and washed at first with a methanol/water mixture (90 : 10 by volume) and then with another methanol/water mixture (70 : 30 by volume). Finally the sample is dried overnight under vacuum at 30–35 °C.

The sample weight can be doubled or tripled, employing the corresponding higher amount of phenylisocyanate. Preferably the sample is adequately disintegrated by hand. 100 ml Erlenmeyer flasks were found suitable for the various treatment steps.

Reference

Procedure of the Fraunhofer Institute of Applied Polymer Research, Teltow-Seehof.

Determination of the *DP* of cellulose in Cuam solution

Preparation of the Cuam solution

The Cuam solution containing 13 g/l Cu and 200 g/l NH_3 is prepared by dissolving freshly precipitated $Cu(OH)_2$ in aqueous ammonia according to the following procedure.

In a 5 l flask, 140 g of copper sulfate (p.a.) are dissolved in about 3 l of H_2O and filtered into a beaker. By adding ca. 70 ml of 25 % aqueous ammonia, $Cu(OH)_2$ is precipitated. After settling of the precipitate a clear solution is decanted and the procedure of settling and decanting is repeated with distilled water until the decanted liquid is free of sulfate ions. For 10 l of Cuam solution, four charges of 140 g of $CuSO_4 \cdot 5H_2O$ have to be processed in this way and 2000 g of NH_3 (in concentrated aqueous solution) are required. The moist sulfate-free $Cu(OH)_2$ is washed with the required amount of ammonia solution in a brown 10 l bottle and dissolved at room temperature. The solution is adjusted to the above-mentioned quantities of 13 g/l Cu and 200 g/l NH_3, with the ammonia content being controlled by acidimetric titration and the copper content being assessed by a complexometric titration with Murexid as the indicator. The solution is stored in a well-closed brown bottle in a dark and cool place.

Determination of the *DP* of cellulose

Samples of pulp or cotton linters are disintegrated without excessive heating. Man-made fiber samples are at first extracted with an ethanol/benzene mixture, 1 : 1 by volume, and then cut to 1–2 mm long pieces. The dry matter content of the sample is determined separately by drying 0.5–1 g of cellulose for 6 h at 105 °C. The sample weight employed for *DP* determination depends on the *DP* range encountered: in the range above $DP = 1000$, 50–100 mg, at $DP < 1000$, 100–200 mg samples are adequate. For dissolving the sample, a brown wide-necked bottle of 100–110 ml capacity is used and the weighed sample is dissolved in 100 ml of the Cuam solution at 20 °C. Pieces of metallic copper are added to minimize the air volume above the solution in the bottle. The mixture is kept for 5 min at 20 °C, then vigorously shaken, and then placed again in a water bath of 20 °C. This procedure is repeated until complete dissolution of the sample. The viscosity measurement is performed in a Doering viscometer (Doering, 1954; capillary length 200 mm, capillary bore width 0.8 mm). The viscosity is calculated from the efflux time of this cellulose solution and of the blank Cuam solution. The cellulose solution in the viscometer can be employed for one measurement only because of possible degradation.

The *DP* is calculated from the specific viscosity $\eta_{spec} = \frac{\eta - \eta_0}{\eta_0}$ according to

$$DP = \frac{2000 \times \eta_{spec}}{c \times (1 + 0.29 \times \eta_{spec})}$$ with c = cellulose concentration in g/l.

The determination should always be performed in duplicate.

References

Doering, H., *Papier (Darmstadt)* **1954**, *8*, 383–387.
Kocevar, F., Pogacnik, H., Povoden, V., *Papier (Darmstadt)* **1957**, *11*, 301–303.

Determination of the acetyl group *DS* of cellulose acetate

0.5 g of dry cellulose acetate is swollen in 25 ml of an acetone/water mixture (1 : 1 by volume) for 24 h at room temperature. Then 12.5 ml of 1 N KOH in ethanol are added, and a complete deacetylation is performed by keeping this mixture for 24 h at room temperature. The excess of alkali is titrated with N/2 aqueous HCl using phenolphthalein as indicator, and an excess of 2 ml of N/2 HCl is added, which is back-titrated after 24 h with N/2 NaOH. From the titration results, the total amount of alkali consumed for saponification of the acetyl groups/g of sample is obtained. Calculation of '% of bound acetic acid' and DS_{Acetyl} is performed according to

$$\%\ bound\ acetic\ acid = \frac{0.107 \times mg\ KOH\ sumed}{weight\ of\ sample}$$

$$DS_{Acetyl} = \frac{162 \times \%AcOH}{6000 - 42 \times \%AcOH}$$

Reference

Procedure of the Fraunhofer Institute of Applied Polymer Research, Teltow-Seehof.

Determination of the carbonyl group content of cellulose samples by oximation

2 g of an air dry sample of known moisture content is suspended in 100 ml of 0.02 N aqueous zinc acetate solution in a 300 ml Erlenmeyer flask under vigorous stirring. After a residence time of 2–6 h at room temperature in the covered flask the liquid is sucked off and the moist sample is immediately and quantitatively returned to the flask and subsequently suspended in 100 ml of the oximation reagent (35 g hydroxylamine hydrochloride, 55 g zinc acetate, 160 ml 1 N NaOH and 1.6 ml glacial acetic acid/l aqueous solution) applying a gentle shaking. After a residence time of 20 h at 20 °C, the liquid is again sucked off through the same sintered-glass disk and twice washed with water. Subsequently the sample is suspended again in the same flask in 100 ml of 0.02 N zinc acetate solution. After 2 h the liquid is again sucked off and the sample is washed with aqueous zinc acetate solution of the same concentration. The moist oximated sample is then immediately subjected to a determination of the nitrogen content by the Kjeldahl method, employing finally a calorimetric determination of the NH_4^+ formed with Nesslers reagent. 1 µmol of nitrogen corresponds to 1 µmol of carbonyl groups in the sample.

Reference

Laboratory procedure of Fraunhofer Institute of Applied Polymer Research.

Determination of the carboxyl group content of cellulose samples by methylene blue sorption

A weighed cellulose sample of known water content up to 0.5 g is suspended in 25 ml of aqueous methylene blue chloride solution (300 mg/l) and 25 ml of borate buffer of pH = 8.5 for 1 h at 20 °C in an 100 ml Erlenmeyer flask and then filtered through a sintered-glass disk. 5 or 10 ml of the filtrate are transferred to a 100 ml calibrated flask. Then 10 ml of 0.1 N HCl and subsequently water, up to 100 ml, are added. Then the methylene blue content of the liquid is determined photometrically, employing a calibration plot, and from the result the total amount of free, i.e. nonsorbed, methylene blue is calculated. The carboxyl group content of the sample is obtained according to

$$mmol\ COOH\ /\ g\ oven\ dry\ sample = \frac{(7.5 - A) \times 0.00313}{E}$$

with A = total amount of free methylene blue in mg
E = weight of oven-dry sample (g)

Reference

Philipp, B., Rehder, W., Lang H. *Papier* **1965**, *19*, 1–10.

Determination of the water retention value of cellulose fiber samples

After disintegration in an attrition mill, 0.5 g of the sample of known water content is weighed to ±0.1 mg into a 100 ml Erlenmeyer flask and suspended in 50 ml of distilled water. The suspension is shaken for 1 h at 20 °C and then transferred to a G3 sintered-glass disk, applying slight suction to remove the adhering water. The sintered-glass disk is then transferred to a suitably adapted centrifuge beaker with a tight cover and centrifuged at 2000 ***g*** (earth gravity acceleration) for 15 min, securing a free efflux of the centrifugate. Subsequently the weight of the moist sample is determined via the difference of mass before and after careful removal of the sample from the sintered-glass disk. The water retention value is calculated according to

$$WRV\,(\%) = \frac{Mass\ of\ moist\ sample - Mass\ of\ dry\ sample}{Mass\ of\ dry\ sample} \times 100$$

The procedure can easily be adapted to other liquids for determining the so-called liquid retention value (LRV), and also the time and the temperature of swelling can be changed over a rather wide range in order to assess a slow course of swelling or the dependency of swelling on swelling temperature.

Reference

Jayme, G., Rothamel, L., *Papier (Darmstadt)* **1948**, *2*, 7–18.

Determination of the *DS* of xanthogenate groups in a fibrous cellulose xanthogenate and in an aqueous cellulose xanthogenate solution

Cellulose content of cellulose xanthogenate solution (viscose)

About 3 g of the xanthogenate solution with 4–10 % cellulose is weighed by difference to the nearest milligram onto a glass plate (10 cm × 10 cm). A second plate is placed on the first one and drawn off in order to obtain a thin film of the solution on each of the plates. The films on the plates are predried at 50 °C for 5–10 min and then placed in a glass dish with 10 % aqueous H_2SO_4 for xanthogenate decomposition. After, the films separated by themselves from the plates subsequent to complete decomposition. They are washed thoroughly with water, dried at 105 °C for at least 3 h, and weighed.

$$\%\ of\ cellulose = \frac{weight\ of\ regenerated\ cellulose \times 100}{weight\ of\ viscose\ sample}$$

Determination of the DS of xanthogenate groups in a fibrous cellulose xanthogenate

A weighed sample of ca. 2 g of fiber xanthogenate is thoroughly washed with ice-cold saturated, aqueous NH_4Cl or $(NH_4)_2SO_4$ solution 6–8 times under kneading with a glass rod, and then placed in a 100 ml flask equipped with a gas inlet and outlet and a funnel with a stopcock. The gas inlet leads in to near the bottom of the flask, the outlet is connected to the gas inlet of a second 100–150 ml flask, leading also to near the bottom, while the gas outlet of this second flask leads to the open air. The second flask contains 50 ml of 2 N ethanolic KOH. 25 ml of 2 N HCl are added to the sample in the first flask and a stream of N_2 is bubbled through the apparatus, while the content of the first flask is heated to boiling for 15 min. The CS_2 liberated by acid decomposition of the xanthogenate is thus bound quantitatively in the second flask as K-ethylxanthogenate. The content of the second flask is neutralized with acetic acid, and the ethylxanthogenate is subsequently titrated with 0.02 N iodine solution.

The cellulose content of the sample is determined by collecting the regenerated cellulose in the first flask on a weighed sintered-glass crucible, washing thoroughly with hot water, drying at 105 °C, and weighing.

Calculation

$$Fraction\ of\ cellulose\ in\ the\ sample: c = \frac{Weight\ of\ cellulose}{Weight\ of\ sample}$$

$$mmol\ xanthogenate\ in\ the\ sample: X = \frac{Consumption\ of\ 0.02\,N\,I_2}{5}$$

$$DS_x\ of\ xanthogenate: \frac{X \times 162}{Weight\ of\ sample \times c \times 1000}$$

Determination of the DS of cellulose xanthogenate in aqueous solution (viscose spinning dope)

The principle of the procedure consists of the decomposition of low molecular sulfidic by-products and the elimination of the CS_2 and H_2S formed in a stream of carbon dioxide and a subsequent iodometric titration of the purified cellulose xanthogenate.

About 1 g of the cellulose xanthogenate solution (viscose) is weighed to the nearest mg into a 250 ml 'washing bottle' filled with 100 ml of ice-cold water and dissolved by swirling. The washing bottle is cooled in an ice bath. For decomposition of by-products a stream of CO_2 is passed through the bottle at a rate of about 2 bubbles per second, until a moist Pb-acetate reagent paper is no longer colored by escaping H_2S. Subsequently, the purified cellulose xanthogenate solution is titrated with an 0.02 N iodine.

Calculation

$$DS_{xanthogenate} = \frac{titrant\ consumption\ in\ ml \times 32.4}{100 \times weight\ of\ sample \times cellulose\ content\ of\ sample\ in\ \%}$$

Reference

Fock, W., *Svensk. Paperstidn.* **1957**, *60*, 911–912.

Determination of the *DS* of carboxymethylcellulose by colloid titration with poly(dimethyldiallylammonium chloride)

The procedure is based on the formation of a water-insoluble polyelectrolyte complex and the abrupt sedimentation (flocculation) of this complex after adding the cationic polyelectrolyte up to this stoichiometric ratio.

A weighed sample corresponding to 20–40 mg of pure sodium carboxymethylcellulose is dissolved in 30 ml of distilled water in a 100 ml beaker under stirring. If necessary the pH value is adjusted to 7 by adding some drops of 1 N aqueous NaOH or 1 N aqueous HCl. By means of a microburette, an aqueous solution of 0.1 M (based on the monomer unit) aqueous polydimethyldiallylammonium chloride is added at a slow rate of about 0.2 ml/min under continuous stirring, until an abrupt flocculation and clarification of the previously turbid solution takes place.

The percentage of pure sodium carboxymethylcellulose in the sample is determined separately with a larger sample of 0.5–1 g by thorough washing with a methanol/water mixture of 80 : 20 by volume (at *DS* values below 1.0) or 90 : 10 (at *DS* values above 1.0), and subsequent drying at 105 °C. The methanol must be free of acid (treatment with Na_2CO_3). In this way the low molecular by-products are removed and the oven-dry weight of the Na-CMC is determined.

To account for a possible small deviation from a 1 : 1 stoichiometry in complex formation, a calibration of the polydimethyldiallylammonium chloride solution is performed by titration of a reference Na-CMC sample in the same *DS* range.

Calculation

$$mmol\ COOH\ /\ g\ of\ Na\ CMC = \frac{T \times m \times f \times 100}{W \times P}$$

where

T = titrant consumption (ml) W = weight of sample

f = calibration factor via reference titration m = molarity of titrant

P = percentage of pure Na-CMC in the sample

$$DS_{CM} = \frac{c \times 162}{1000 - 80 \times c}$$ where c = mmol COOH/g

Reference

Hong, L.Tr., Borrmeister, B., Dautzenberg, H., Philipp, B., *Zellst. Pap.* **1978**, *5*, 207–210.

Determination of *DS* of tritylcellulose (gravimetric method)

10 g of trityl cellulose (dried for 24 h at 70 °C under vacuum), are dissolved under stirring in 10 ml of concentrated sulfuric acid. After complete dissolution a clear and dark-tone (colored) solution is obtained. To the solution distilled water is carefully added until the solution changes via dark green and yellow to gray. Then 90 ml of water are gradually added to precipitate triphenylmethanol. The precipitate was filtered, washed with water free of sulfate ions and dried to constant weight.

$$\% \text{ trityl} = \frac{\text{weight of triphenylmethanol} \cdot 243 \cdot 100}{\text{sample weight} \cdot 260}$$

$$\text{DS} = \frac{1.62 \cdot (\% \text{ trityl})}{243 - 2.42 \cdot (\% \text{ trityl})}$$

Green, J.W., *Methods in Carbohydrate Chemistry*, Whistler, R.L., Green, J.W., BeMiller, J.N., Wolfrom, M.L. (Eds.), New York: Academic Press, **1963**.

Polymer modification for structure analysis of thexyldimethylsilyl-celluloses by NMR spectroscopy and HPLC

Permethylation

1 g of thexyldimethylsilylcellulose was dissolved in 30 ml of tetrahydrofuran (THF) and treated with sodium hydride (10 mol/mol of modified AGU). After addition of the same molar amount of methyl iodide, the mixture was stirred for 1 day at 25°C and 2 days at 50°C. Separation of white precipitate was carried out by centrifugation, and the solution was poured into buffer solution (pH 7). The product was isolated, washed several times with water and dried under vacuum over potassium hydroxide, first at 25°C then at 50°C.

Complete methylation is indicated by the absence of the infrared absorption in the ν(OH) range.

Desilylation

0.5 g of the permethylated polymer was dissolved in 10 ml of THF and treated with tetrabutylammonium fluoride (2 mol/mol of Si groups). After stirring for 1 day at 50°C, it was poured into diethyl ether/hexane (1:1; v/v), washed with hexane and dried at 25°C and 0.1 Torr. It is not necessary to remove all solvent traces.

Peracetylation

The obtained methylcellulose was dissolved in 10 ml of pyridine and treated with 10 ml of acetic acid anhydride. The mixture was stirred for 24 h at 25°C and 4 h at 100°C. After cooling down to room temperature, the mixture was poured into 200 ml of buffer solution (pH 7) containing 10% sodium hydrogen carbonate. The polymer was separated, and washed and dried as described.

Complete acetylation is indicated by the absence of the infrared absorption in the ν(OH) range. For NMR measurements, a 5–10% solution in deuterochloroform was used.

FTIR (KBr): 2941–2828 cm^{-1} ν(CH_2, CH_3); 1745 cm^{-1} ν(C=O); 1453 cm^{-1} δ (CH_2, CH_3); 1236 cm^{-1} ν(C-O-C, Ester); 1083 cm^{-1} ν(C-O-C, AGU)

Chain degradation of the permethylated polymers to the corresponding methyl glucoses

0.3–0.5 g of the permethylated thexyldimethylsilylcellulose was treated with 10 ml of 4 N trifluoroacetic acid and allowed to stand for 1 day at 25°C. 10 ml of water was added and the mixture was heated at 120°C for 4 h. The acid was evaporated on a rotary evaporator, and water was distilled off until the mixture became neutral, and the water was removed completely. The residual mixture of methyl glucoses was stored under dry conditions, and an aqueous solution was used for HPLC analysis.

Koschella, A., Klemm, D., *Macromol. Symp.* **1997**, *120*, 115–125.

Alkali resistance of cellulosic materials (Zellcheming* standard method IV/39/67)

The alkali resistance *R* is the percentage of dry matter of a cellulose material which is insoluble in aqueous NaOH of specified concentration at 20 °C. For determining the alkali resistance of wood pulp, a very precise standardized procedure has been elaborated by Zellcheming, which can be adapted to other cellulosic materials and is subsequently reprinted in its original text.

Test principle

The pulp sample is defibered under specified conditions in sodium hydroxide solution of chosen concentration and temperature. The insoluble fraction is filtered off, washed with sodium hydroxide solution of the same concentration and temperature, then acidified with acetic acid, washed with water, dried and weighed.

Test equipment

Apparatus:

– An analytical balance, with an accuracy of ±0.0002 g.
– A 250 ml flat-bottomed beaker of alkali-resistant material, with a suitable watch glass as cover.

* Verein Zellcheming, Berliner Alle 56, D-64295 Darmstadt, Germany

– A stirring rod of 15 mm diameter with flattened ends and of alkali-resistant material.
– A conical filtering device with a capacity of 80–100 ml, an inner diameter at the bottom of 30 mm, and at the top of 50 mm, a height of approximately 60 mm, consisting of alkali-resistant material (alternatively, a sintered-glass filter of pore size G1 and a nominal capacity of 125–500 ml may be used if special care is taken that the fritted filter disc is in a satisfactory condition).
– A stainless steel gauze with a pore size of 0.3 mm (DIN 4188), 29.5 mm in diameter, soldered along the rim.
– A thermostat, adjustable to 20±0.2 °C suitable for beakers, a storage bottle with sodium hydroxide solution and a suction flask.
– A suction flask, with a capacity of 0.5 or 1 l.
– A pair of tweezers.
– A weighing glass.
– A drying oven, adjustable to 105±2 °C (DIN 50011).
– A desiccator (DIN 12 490 and 12 491).

Reagents:
Sodium hydroxide stock solution, containing less than 1g/l of sodium carbonate, is prepared by dissolving 500 g of sodium hydroxide of analytical grade in 500 ml of distilled water (if necessary allow to settle and filter). Sodium hydroxide solutions of specified concentrations are prepared by diluting appropriate volumes of the stock solution to the following concentrations.

18.0±0.1 g of NaOH per 100 g of solution, equivalent to 215.5±0.1 g of NaOH per liter.
(Density at 20 °C: 1.1972 g/ml)

10.0±0.1 g of NaOH per 100 g of solution, equivalent to 110.9±0.1 g of NaOH per liter.
(Density at 20 °C: 1.1089 g/ml)

The dilute sodium hydroxide solutions should be stored in polyethylene bottles.

Acetic acid, 20 % solution by weight
(Density 1.026 g/ml).

Procedure
Preparation of sample:
Air-dry pulp in sheet form should be torn into pieces of approximately 5 mm × 5 mm. If the sample is difficult to defiber, split the test pieces by means of tweezers. A preliminary mechanical disintegration, which is detrimental to the fibers, is not allowed.

Pulp in wet sheet form should be dried at a maximum temperature of 60 °C. If the pulp is in slush form, remove the water by suction, taking care not to lose any fibers, press between filter paper and dry at a maximum temperature of 60 °C.

Before weighing, the sample should be conditioned for at least 20 min in the surrounding air near the balance.

Weighing out the sample:
Weigh out approximately 2.5 g of the sample to the nearest 1 mg. Two further quantities should be weighed out at the same time for the determination of the dry matter content (T %) at 105±2 °C (according to data sheet IV/42/67 or DIN 54 352 E).

Alkali treatment:
During the action of sodium hydroxide on the pulp, the mixture must be kept at the specified constant temperature.

At least two parallel determinations should be carried out on each sample. Transfer the weighed sample to a 250 ml beaker, add 25 ml of the sodium hydroxide solution of known concentration which has previously been adjusted to 20±0.2 °C. Place the beaker in a bath of constant temperature for 3 min to allow the pulp to swell. Thoroughly defiber the pulp by stirring and macerating with a rod for at least 3 min, with a macerating rate of 2 strokes per second, until completely defibered. Add another 25 ml of sodium hydroxide solution of the same concentration and temperature, stir until the suspension is uniform and finally dilute the suspension by adding 100 ml of sodium hydroxide solution of the same concentration and temperature. Cover the beaker with a watch glass and place it in the water bath at constant temperature at 20±0.2 °C for 60 min, measured from the first addition of sodium hydroxide. After the 60 min, stir the suspension again and transfer in portions to the filtering device fitted on the dry filter flask, which has been adjusted to 20±0.2 °C in the water bath. After this, apply the suction immediately.

Apply suction only as long as the fiber-mat is still covered with liquid, thus preventing air from being sucked through the mat. Use the first filtrate obtained for rinsing the beaker and filter-funnel and filter again through the slightly pressed fiber-mat in order to collect all fibers. Then wash the fiber-mat with two 25 ml portions of sodium hydroxide of the same temperature and concentration, using only a slight suction to avoid air being sucked through the fiber-mat. Finally apply full suction briefly.

The time for filtering and washing should not exceed 20 min.

Final treatment:

Compress the fiber-pad, especially at the edges, and cover with 200 ml of dilute acetic acid in portions, and allow to pass through the fiber-mat slowly without the use of suction. Then suck off the acid completely and wash the fiber-mat with hot distilled water until the filtrate is free of acid. During the final washing cover the filter with the hand to ensure that a vacuum is formed above the fiber-mat. Quickly release the vacuum in the suction flask in order to lift the fiber-mat. Transfer the fiber-pad, together with any fibers adhering to the inside of the filter device or the gauze, to the weighing glass by means of the tweezers. Now place the open weighing glass, together with the cover, in the drying oven and dry to a constant weight at a temperature of 105±2 °C, which generally takes about 6 h. Allow the closed weighing glass to cool in a desiccator and determine the weight of the alkali-insoluble fraction to the nearest 1 mg, after briefly raising the cover to equalize the air pressure.

Test report

Calculate the alkali resistance as a percentage of the original sample as follows:

$$R = \frac{m \times 100}{E \times T} \times 100\%$$

where
m = weight of alkali-insoluble fraction (g)
E = weight of sample (g)
T = oven-dry weight of the original pulp sample (%).

Report the alkali resistance as the mean of the parallel determination to the first decimal place using the symbols R_{18}, R_{10}, R_c, etc.

The results of two parallel determinations should be carried out and the results evaluated statistically.

Example:
2.525 g of air-dry pulp (E) are weighed out. The dry matter content of this pulp is found to be 92.8 % (T) and the weight of the dried fiber residue is 2.156 g (m).

$$R = \frac{m \times 100}{E \times T} \times 100 = \frac{2.156 \times 100}{2.525 \times 92.8} \times 100 = 92.0\%.$$

References

Bartunek, R., *Papier (Darmstadt)* **1952**, *6*, 120.
Doering, H., *Papier (Darmstadt)* **1948**, *2*, 354.
Doering, H., *Papier (Darmstadt)* **1949**, *3*, 37.
Doering, H., *Papier (Darmstadt)* **1951**, *5*, 127.
Vieweg, R., *Papierfabrikant* **1934**, *32*, 521.

Alkali solubility of cellulose materials (Zellcheming standard method IV/44/67)

The alkali solubility *S* is defined as the percentage of dry matter of the cellulose material which is soluble in aqueous NaOH of specified concentration at 20 °C, and which can be oxidized with dichromate in sulfuric acid. For determining the alkali solubility of wood pulp, a precise standardized procedure has been elaborated by Zellcheming, which can be adapted to other cellulosic materials, and which is subsequently reprinted in its original text.

Test principle

The pulp sample is treated under specified conditions with sodium hydroxide solution of a specified concentration at 20±0.2 °C for 1 h. After this time the sodium hydroxide solution is filtered off. In an aliquot of the filtrate, the dissolved organic matter is oxidized with dichromate in sulfuric acid. Excess dichromate is determined volumetrically with iron(II)-ammonium sulfate solution.

Test equipment

Apparatus:

– An analytical balance, with an accuracy of ±0.0002 g.
– Stirring equipment, with a propeller-type agitator made of stainless steel or other non-corrosive material. The angle of the blades should be adjusted so that air is not introduced into the pulp suspension during stirring. A satisfactory motor is 1/50 hp, running at about 1450–1700 r.p.m..
– A thermostat, adjustable to 20±0.2 °C, suitable for beakers, a storage bottle with sodium hydroxide solution and a suction flask.
– A 250 ml flat-bottomed beaker of alkali-resistant material, e.g. polyethylene, with a suitable watch glass as cover.
– Filtering crucibles of sintered-glass, with a pore size of G3, made of alkali-resistant material and a capacity of 500 ml.
– A suction flask, with a capacity of 0.5 or 1 l.
– Pipettes, 5, 10, 20 and 100 ml (DIN 12 690).
– Conical flasks, 250 ml (DIN 12 380).
– Burette, 50 ml (DIN 12 700 or 12 701).

Reagents:

Sodium hydroxide solution of specified concentration containing less than 1 g/l of sodium carbonate, e.g.:

18±1 % of NaOH per 100 g of solution, equivalent to 215.5±1 g NaOH per liter.
10±1 % of NaOH per 100 g of solution, equivalent to

110.9±1 g of NaOH per liter.
5±0.05 % of NaOH per 100 g of solution, equivalent to
52.7±0.5 g NaOH per liter.
(Density at 20 °C: 1.052 g/ml)

Prepare the sodium hydroxide stock solution, containing less than 1 g/l of sodium carbonate, by dissolving 500 g of sodium hydroxide of analytical grade in 500 ml of distilled water (if necessary allow to settle and filter). The stock and the dilute sodium hydroxide solutions should be stored in polyethylene bottles. Check by titration with standard acid and, if necessary, adjust to appropriate concentration.

Potassium dichromate solution, 0.067 M (= 0.4 N), in 2.7 M sulfuric acid: Dissolve 20 g of $K_2Cr_2O_7$ and 150 ml of sulfuric acid (ρ = 1.84) and make up to 1 l.

Iron(II)-ammonium sulfate solution, ca. 0.1 N: Normality known with an accuracy of ±0.0002. Dissolve about 40 g of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and 10 ml of sulfuric acid (ρ = 1.84) and make up to 1 l. This solution is not stable and its titer should be checked every day.

Ferroin indicator solution: 1.5 g of 1:1 phenanthroline hydrochloride, $C_{12}H_6N_2.HCl.H_2O$ and 0.7 g of iron(II) sulfate, $FeSO_4 \cdot 7H_2O$ per 100 ml of solution.

Procedure

Preparation of sample:

Tear air-dry pulp in sheet form into pieces of approximately 5 mm × 5 mm. If the sample is difficult to defiber, split the test pieces by means of tweezers. A preliminary mechanical disintegration, which is detrimental to the fibers, is not allowed.

Pulp in wet sheet form should be dried at a maximum temperature of 60 °C.

If the pulp is in slush form, remove the water by suction taking care not to lose any fibers, press between filter paper and dry at a maximum temperature of 60 °C.

Before weighing, the sample should be conditioned for at least 20 min in the surrounding air near the balance.

Determination of the dry matter content:

Carry out at least two parallel determinations of the dry matter content (T %) according to Standard IV/42/67 or DIN 54 352.

Weighing the sample:

Weigh to the nearest 0.005 g, the equivalent of approximately 1.5 g of dried (105 °C).

Alkali treatment:
During the action of sodium hydroxide on the pulp, the mixture must be kept at constant temperature as specified. Transfer the weighed sample to a 250 ml beaker adjusted to 20.0±0.2 °C by being placed in the constant-temperature bath.

With a pipette add 100 ml of the sodium hydroxide solution of known concentration which has previously been adjusted to 20±0.2 °C (volume V_1). After allowing the pulp to swell for 2 min, stir the suspension in the beaker for 3 min or until the pulp is completely disintegrated, observing that no air is sucked in during stirring. Lift the stirrer from the reaction vessel. Some fibers and residues of the solution may remain on the stirrer when it is removed. Maintain the reaction mixture at 20±0.2 °C for a period of 60 min beginning from the time the pulp was brought into contact with the sodium hydroxide solution.

After 60 min, stir the slurry with a glass rod, and filter with slight suction through the sintered-glass crucible or funnel, avoiding any passage of air through the fiber mat. Reject the first 10–20 ml of the filtrate and collect the next 40–50 ml in a clean bottle or flask for testing. After use, the filters should be washed immediately with a solution of potassium dichromate in sulfuric acid and thereafter rinsed with distilled water.

Wet oxidation:
Transfer with a pipette 10.0 ml (volume V_2) of the filtrate to a 250 ml conical flask. Add with a pipette 10.0 ml of potassium dichromate solution and then carefully, with swirling, 30 ml of concentrated sulfuric acid. Check that the temperature rises to 125–130 °C and remains above 120 °C for 10 min to ensure complete oxidation. Cool the solution to room temperature.

Titration with ferroin as indicator:
To the cold solution, add 50 ml of distilled water. Cool again, add two drops of ferroin indicator and titrate with the freshly standardized iron(II)-ammonium sulfate solution until the color turns purple (volume *a*).

Carry out at the same time a blank test, substituting 10 ml of the chosen sodium hydroxide solution for the filtrate and using approximately the same temperature and time to complete the titration (volume *b*). Alternatively the determination may be carried out as a potentiometric titration.

Number of determinations
Carry out two parallel determinations on each sample. The results of two parallel determinations should agree within 0.3 %, otherwise both determinations are to be repeated.

Calculation and result

Calculate the alkali resistance as percentage by weight:

$$S_c = \frac{10 \times 6.85(b-a) \times N \times V_1}{g \times V_2 \times T}$$

where

S_c = alkali solubility according to this standard (%), where c denotes the concentration of the sodium hydroxide used (% by weight).

a = volume of 0.1 N iron(II)-ammonium sulfate solution used for the titration of test solution (ml).

b = volume of 0.1 N iron(II)-ammonium sulfate solution used for the titration of the blank (ml).

N = normality of the iron(II)-ammonium sulfate solution to 0.0002.

g = weight of the pulp (g).

T = dry matter content of the original pulp sample (% by weight) according to Standard IV/42/67 or DIN 54 352.

V_1 = volume of sodium hydroxide solution used in the alkali treatment (ml).

V_2 = volume of filtrate used for the wet oxidation and titration (ml).

6.85 = empirical factor indicating the amount of cellulose in mg equivalent to one milliequivalent of potassium dichromate. Theoretically, 1 milliequivalent of potassium dichromate corresponds to 6.75 mg of cellulose or other hexosans, and to 6.60 mg of pentosans. In general the alkali-soluble components of pulp consume less oxidant than is theoretically expected. Therefore, the somewhat higher factor of 6.85 mg, is internationally adopted and applied in this method.

Test report

1. Alkali solubility, S_c in % by weight to 0.1 %, single values and arithmetic mean. Insert the concentration of the sodium hydroxide solution used in % by weight as an index, e.g. S_{18}, S_{10}, etc.
2. Type and description of the sample.
3. Any deviations from the standard testing method.
4. Date of testing.

Example of calculation

Weight of air dry sample (g)	1.735 g
Dry matter content of the sample (T)	92.4 %
Volume of iron(II)-ammonium sulfate consumed in the blank (b)	41.4 ml
Volume of iron(II)-ammonium sulfate solution consumed in the test (a)	15.5 ml
Normality of iron(II)-ammonium sulfate solution (N)	0.1005

Volume of sodium hydroxide solution in alkali treatment (V_1)	100.0 ml
Volume of filtrate used in the titration (V_2)	10.0 ml

Alkali solubility

$$(S_c) = \frac{10 \times 6.85(41.1 - 15.5) \times 0.1005 \times 100}{1.735 \times 10.0 \times 92.4} = 11.0\%$$

Subject index

Comprehensive Cellulose Chemistry; Volume 1: Fundamentals and Analytical Methods
D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht

ISBN: 3-527-29413-9

Typical cellulose materials of commercial relevance

Material	Lattice type	DP range (Cuam)	Fiber dimensions length (mm)	width (μm)
Cotton	I	> 3000	10—60	10—40
Ramie	I	6000—7000	130—260	10—40
Flax	I	7000—9000	20—40	10—20
Cotton linters (scoured and bleached)	I	800—2600	5	40
Softwood pulp				
paper grade	I	> 1000	3—6	20—50
dissolving grade	I	300—1700	3—6	20—50
Hardwood pulp				
paper grade	I	> 1000	1—4	50—200
dissolving grade	I	300—1000	1—4	50—200
Cellulose powder (hydrolized spruce pulp)	I	150—300	0.08—0.12	10
Viscose rayon				
staple	II	250—450	30—80	15—30
textile grade	II	260—300	-	15—30
cord grade	II/IV	300—450	-	15—30

Comprehensive Cellulose Chemistry; Volume 1: Fundamentals and Analytical Methods
D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht

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Selected solvents for cellulose

Non-derivatizing

N,N-Dimethylacetamide/LiCl
N-Methylpyrrolidone/LiCl
N-Methylmorpholine-*N*-oxide
Ethylenediamine/SO_2/dimethylsulfoxide
Tetraalkylammonium halides/dimethylsulfoxide
Aqueous tetraalkylammonium hydroxides

Metal complexes

Cuam	Cuprammonium hydroxide
Cuen	Cupriethylenediamine chelate
Cadoxen	Cadmiumethylenediamine chelate
FeTNa	Sodium salt of ferric tartaric acid

Derivatizing media

$CS_2/NaOH/H_2O$
$CF_3COOH/(CF_3CO)_2O$
$HCOOH/H_3PO_4$
$(CH_2O)_x/(CH_3)_2SO$
$CCl_3CHO/(CH_3)_2SO/N(C_2H_5)_3$

^{13}C NMR signals of cellulose

Solvent	δ (ppm)					
	C-1	C-2	C-3	C-4	C-5	C-6
$NaOH/D_2O$	104.5	74.7	76.3	79.8	76.2	61.5
N,N-Dimethylacetamide/LiCl	103.8	74.9	76.6	79.8	76.7	60.0
Benzyltrimethylammonium hydroxide/D_2O	104.7	74.9	76.7	80.1	76.4	61.8
Cadoxen	103.8	74.9	76.7	78.9	76.4	61.8

Important physical data of cellulose

Property	Native fibre	Manmade fibre
DP (Cuam)	10^3-10^4	250-450
X-ray crystallinity (%)	50-75	25-40
Density (g/cm^3)	1.53-1.89	1.49-1.55
Breaking strength (cN/tex) dry	26-50	14-61
wet	26-50	2-58
Elongation at break (%) dry	2-10	7-30
wet	2-11	8-40
Elastic modulus (cN/tex) dry	370-2200	265-1950
Spec. resistance at 65% rel. humidity (Ωcm)	10^5-10^9	10^{10}-10^{15}
Dielectric constant ε at 65% rel. humidity	3-6 (cotton)	3-7 (rayon)
Refractive index (parallel)	1.573-1.595 (cotton)	1.529-1.571
(perpendicular)	1.527-1.534 (cotton)	1.509-1.534
Coefficient of thermal expansion (K^{-1})	ca. 10^{-4}	ca. 10^{-5}
Thermal conductivity (Wm/K)	0.071 (cotton)	0.054-0.07 (rayon)
Spec. heat capacity C_p (J/g K)	1.32-1.78	1.36-1.60
Assumed melting point (°C)	> 400	> 400
Thermal decomposition point (°C)	180-250	180-250
Water vapor regain at 65% rel. humidity (%)	7-8	12-14
Water retention value (%)	50-80	70-140
[η]-*DP*-relation of dissolved cellulose in		
Cuam	$[\eta] = 1.37 \times DP^{0.72}$	
Cuen	$[\eta] = 1.75 \times DP^{0.69}$	
Cadoxen	$[\eta] = 1.67 \times DP^{0.71}$	
FeTNa	$[\eta] = 4.85 \times DP^{0.61}$	